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Development of Coated Fuel Particles

KFA Contributions within the frame of the German High Temperature Reactor Fuel Development Program

by

H. Nickel

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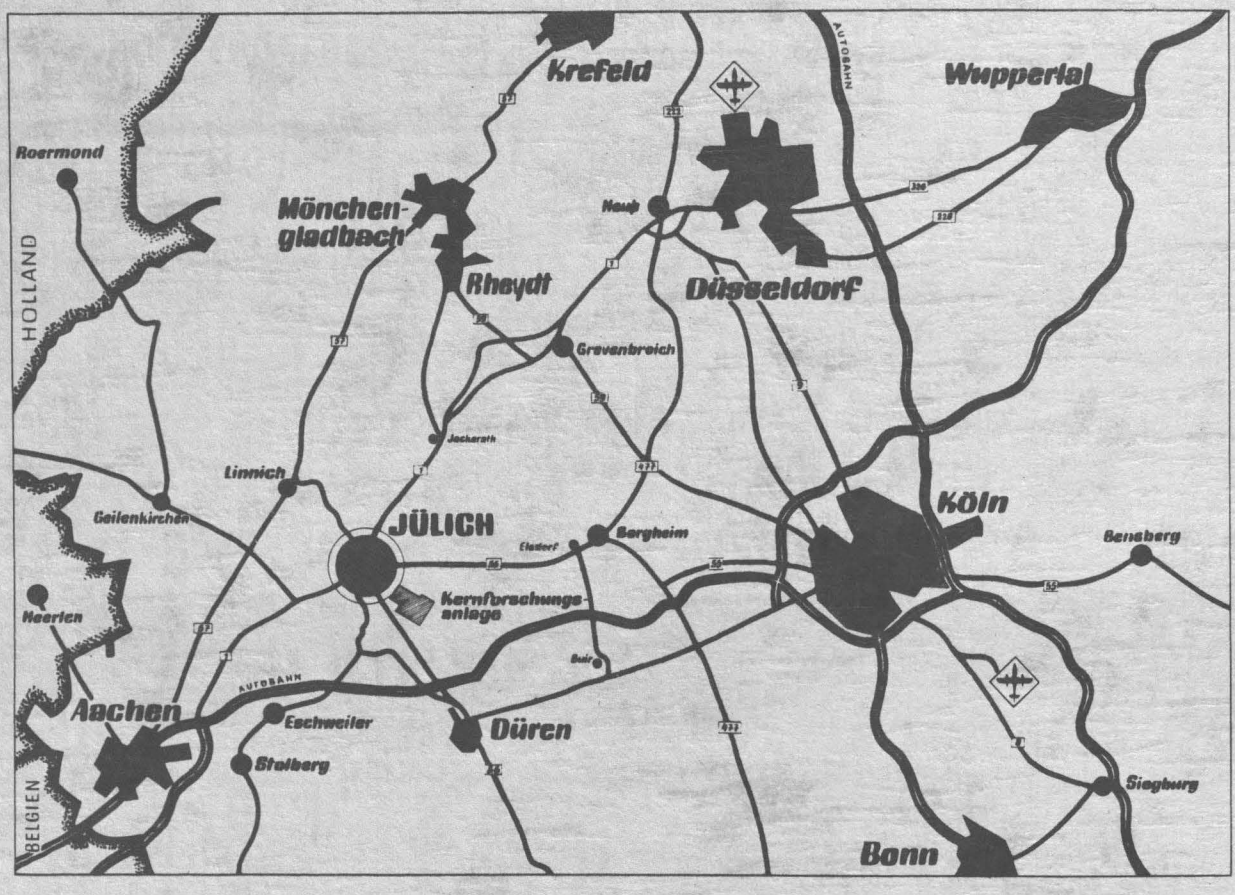

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Contents

1. Introduction

Due to the formation of radioactive fission products in the nuclear fission process, safety regulations for the operation of nuclear power plants are much more severe than for conventional stations. The prevention of fission product release from fuel elements is therefore one of the main problems of nuclear power production. Whereas the fuel in water or liquid metal cooled reactors is contained in a metal cladding, the only material which can be used as fuel containment in a helium cooled high temperature reactor (HTR) is graphite. Industrial graphites, however, generally display a high permeability for fission products. That leads to the use of coated particles to load feed and breed material into the fuel elements of HTR's. They consist of a fuel kernel, of carbide or oxide of uranium or uranium plus thorium and as a containment or "cladding" of this kernel several different layers of pyrocarbon (PyC) and eventually an additional layer of silicon carbide (SiC). The layers are deposited from the gaseous phase by thermal disintegration of various hydrocarbons resp. chlormethylsilanes. To retain fission products these coatings must remain mechanically stable. They have to withstand the swelling of the kernel with increasing burn up and the pressure of the fission gases, which can be as high as 1oo atmospheres at high burn ups; in addition the coatings have to be themselves radiation resistant and impermeable for fission products under reactor operation conditions - i.e. behave as a diffusion barrier. Although coated particles have proved good over some years in operating high temperature reactors (Tab. 1), there are several reasons for continuing their development.

1.) The specification data for burn-up, maximum fast neutron flux and maximum power rating for the existing high temperature reactors are significantly lower than for the prototyp plants planned or under construction as shown by the comparison of AVR and THTR (Thorium High Temperature Reactor) plant data in table 2.

2.) In view of the HHT Project (High Temperature Reactor with a Helium Turbine), aiming at the development of a high temperature reactor with a helium turbine in the primary

circuit (a so-called one-circuit-plant), still higher demands concerning the fission products retention are put forward than for HT-reactors, the concepts of which are based on a two-circuit-plant system.

Reactor	Power therm. (MW)	Power electr. (MW)	Helium-temp. (°C)	Fuel element shape	critical since
Peach Bottom/USA	115	4o	75o	prismatic, pin-type	March 1966
Dragon/England	2o	-	75o	prismatic, pin-type	August 1964
AVR-Jülich	45	15	85o	spherical ball (6 cmØ)	August 1966

Table 1: He-cooled High Temperature Reactors in operation

	AVR	THTR
Max. burn-up	9 % fima	14 % fima
Max. fast neutron dose (E ≥ o,1 MeV)	$2.1o^{21}(n.cm^{-2})$	$6,4.1o^{21}(n.cm^{-2})$
Max. Power rate per fuel element	2,4 kW	4,3 kW

Table 2: Some data of spherical fuel elements for the AVR and THTR

The material development for high temperature reactors in Germany is performed in collaboration with the firms BBK (Brown-Boveri Krupp), GHH (Gutehoffnungshütte), NUKEM (Nuclear Chemie und - Metallurgie GmbH) and KFA Jülich. This paper deals especially with the work done by KFA particularly in the Institut **für Reaktorwerkstoffe (IRW).**

The coated particles in the spherical and pin type fuel elements are not loose, but for reasons of better heat conductivity and for higher safety they form solid compacts with the graphite matrix. **Thus, the development of coated particles** can not be viewed under the aspects of the particles alone but has to be performed within the frame of the whole fuel element.

For the **design** of a reactor naturally only fuel elements proved successfully in thorough reactor irradiation tests are acceptable. Therefore in the frame of the HTR fuel element development an extensive irradiation program has been carried out on either loose coated particles or fuel element balls or prismatic compacts.

The present report deals with the latest state of the following developments:

1.) Production process for fuel kernels.
2.) Coating of fuel kernel with PyC and SiC with defined structures and properties.
3.) Coated particle compacts for prismatic fuel elements.
4.) Irradiation of coated particles.

2. Fabrication of fuel kernels

Two groups of processes for the production of fuel kernels can be distinguished, depending if the process starts from powders or from solutions of the uranium-thorium compounds used:

1.) powder metallurgical processes
2.) liquid processes.

The powder metallurgical processes are in use since a long time on a technical scale. The first charges of the operational HT reactor AVR, Peach-Bottom and DRAGON contain coated particles with carbide kernels produced by powder metallurgical producers. UO_2 resp. U_3O_8 alone or in mixture with ThO_2 is granulated and by adding carbon powder and a binder green particles are obtained. These are embedded in graphite powder and melted at temperature above 2500°C to form dicarbides[1]. By burning-off the carbon of green particles in air oxide kernels of uranium or uranium-thorium can be obtained, which are sintered in a hydrogen atmosphere at 1700°C. Only porous kernels can be produced with a maximum density of 90 % of the theoretical density and a shell like structure[2]. It is an obvious disadvantage of the powder metallurgical process that no dense oxide kernels can be produced. Moreover the process starts with heavy metal oxides, requiring an additional conversion step, because uranium and thorium compounds of nuclear

of nuclear purity are almost exclusively available as solutions of salts. The same applies with respect to reprocessing processes, where the uranium from burned-out fuel is obtained in the form of uranyl solutions.
The liquid processes offer therefore a substantial advantage. Furthermore, the chemical processes can produce oxide kernels of any desired composition, pore size distribution and density and the fabrication of carbide kernels is also possible.

2.1 Sol-Gel-processes

From the processes, starting from aquous heavy metal solutions the so-called sol-gel processes have gained a particular importance. In figure 1 the flow sheets of sol-gel processes for the production of spherical uranium dioxide kernels developed at ORNL (USA)[3-7], CNEN (Italy)[8-1o] and KFA are compared.
The first two processes are used on a technical scale (5-1o kg/day), the feasibility of the KFA process was demonstrated with a pilot plant (o,5 kg per day). All three processes are suited for the production of either UO_2 or $(Th,U)O_2$ kernels.
Before discribing the details of the KFA-process and the differences between the three processes, the main principle of the sol-gel process will be explained.
In the sol-gel process a colloidal liquid solution of the fuel material - the sol - is dropped into a liquid practically unmiscable with water. The spherical droplets are solidified by a gelation process and can be dried and sintered to obtain fuel kernels.
The colloidal solution contains oxide of the fuel material in the form of very small crystallites which after gelation form a stable structure, soaked with water.
Fig. 2 shows electromicroscopical photographs, on the left of an uranium dioxide-sol and on the right the interconnected crystallites of an uranium gel. The average size of the crystallites is approximately 5o Å. This extreme fine distribution in the colloidal form **makes it** possible to obtain oxides with nearly theoretical density by sintering at 12oo°C without application of pressure. Sintering for example fine granulated thorium oxide powder, however, leads to products of only 95 % of the theoretical denstiy, even at sintering temperatures of 2ooo°C.

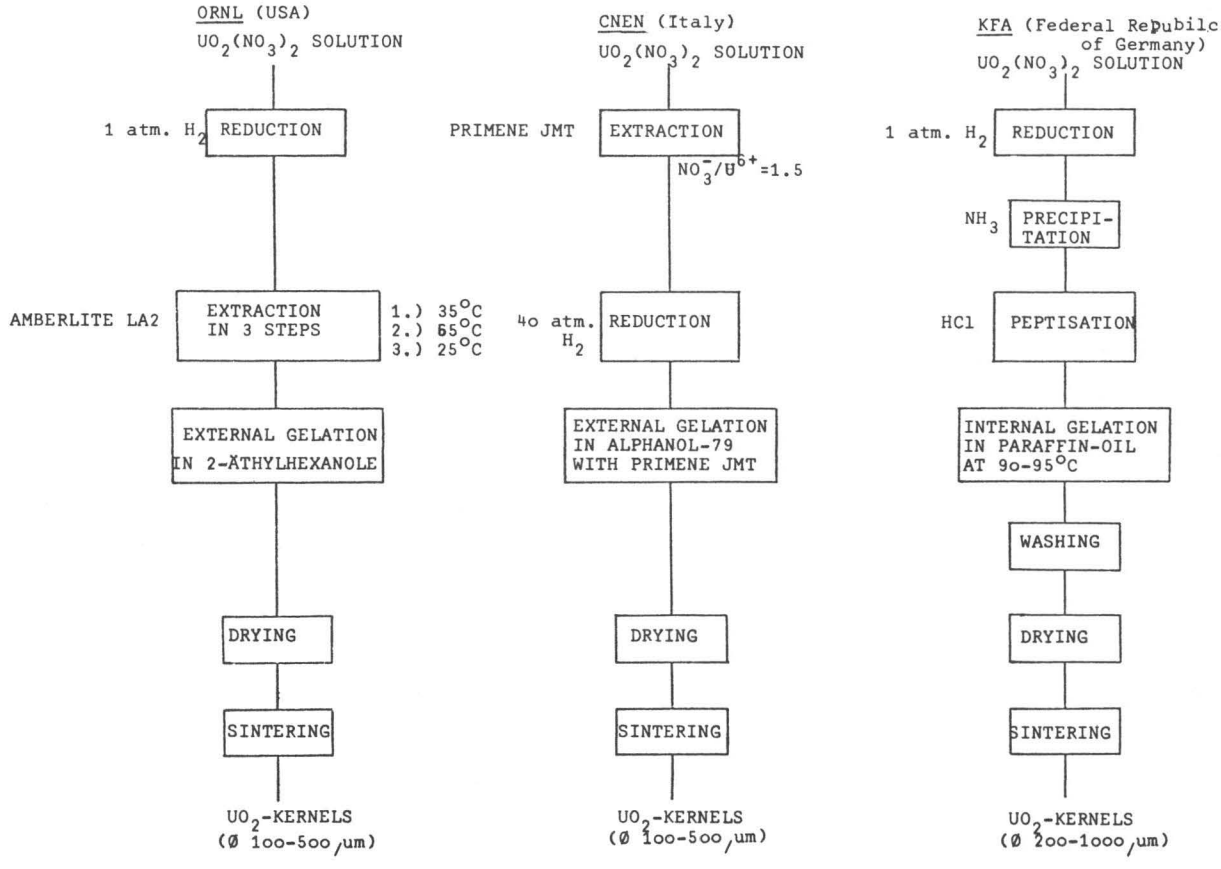
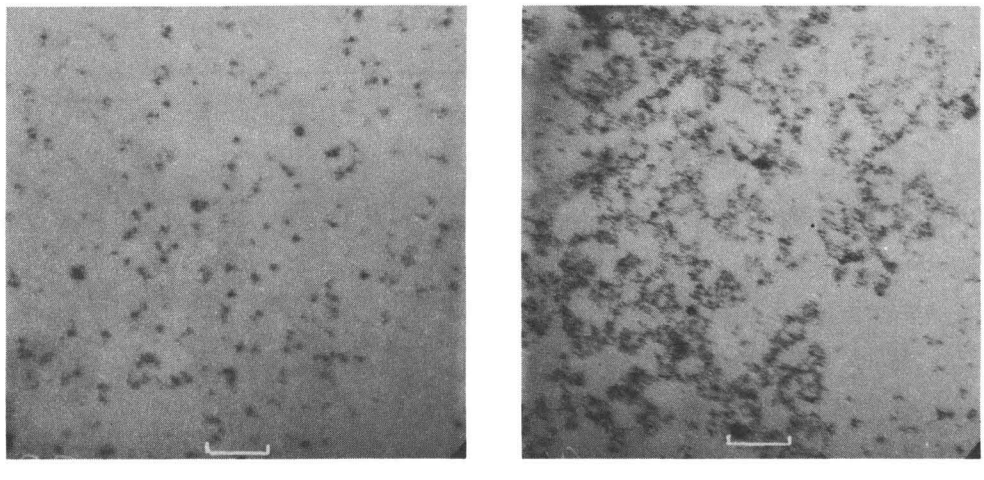


Fig. 1: Flow shemes of ORNL, CNEN and KFA sol-gel processes for production of UO_2 kernels.



1000 Å

Fig. 2: Electromicroscopical photograph of an UO_2-sol (left) and an UO_2-gel (right).

During gelation, i.e. the **conversion of a sol into a geometrical** stable gel either the average distance between the colloidal particles is reduced to an extend that the surface tension exceeds the electrostatical repulsion of the positively charged particles (gelation process 1), or the electrostatical charge of the particles in neutralized (gelation process 2). The first tpye of gelation occurs during the "external gelation", the second during the internal gelation. **A flowsheet of both processes is shown in fig.3.** The external gelation is based upon the fact that water is extracted from the droplets, i.e. concentration increase in the sol, whereas the internal gelation is caused by a chemical reaction inside the sol droplets, starting with increasing temperature. The chemical reaction is the formation of ammonia by the thermal decomposition of hexamethylentetramine; the gelation takes place as a consequence of the p_H increase during the reaction. The external gelation, which is the basis of the ORNL and CNEN-processes is a very slowly running reaction. It is therefore not possible to obtain spherical particles with diameters greater than 500-600 µm, after sintering. The internal gelation however is a very fast and uniformly proceeding reaction and renders possible the production of spherical and highly dense UO_2 resp. $(U,Th)O_2$ kernels with diameters of more than 800 µm.

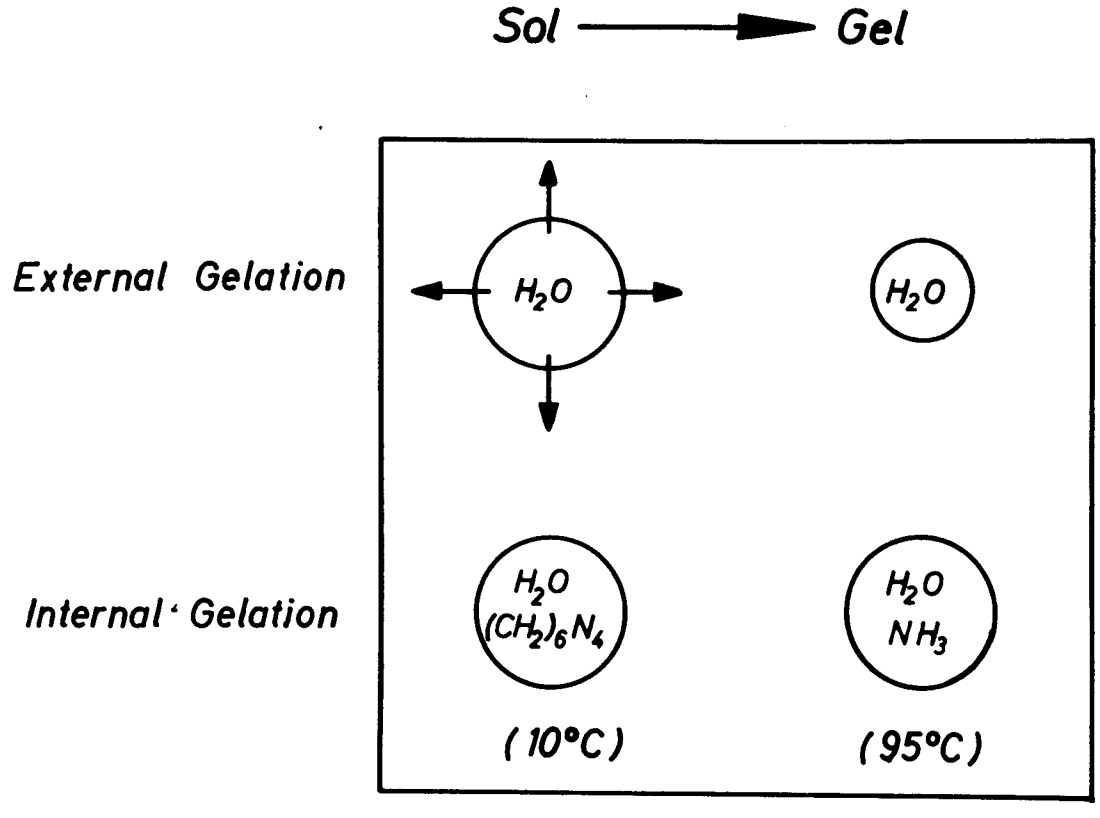


Fig. 3: External and internal gelation (schematically)

2.1.1 KFA Sol-Gel-process

The KFA sol-gel process was originally developed for the fabrication of oxide and carbide feed and breed particles with well known porperties for out of pile experiments. For these experiments oxide kernels with high density, diameters ranging from 150 to 850 µm and variable porosity are desired. The flow-sheet of the KFA process is given in fig. 1. The process starts with an aquous Uranyl(VI) nitrate or chloride solution. This solution is catalytically reduced with hydrogen forming uranium(IV) which is precipitated in a second step as uranium dioxide hydrate by addition of ammonia. For the production of ThO_2 or $(U,Th)O_2$ kernels this reduction step can be omitted if the U/Th ratio is less than 25 wt-%. The decision step is the conversion of the washed uranium dioxide hydrates to the uranium dioxide sol, the peptisation. It has been proved that UO_2-sol produced by the American UO_2-specification could not be used for internal gelation because of its formic acid content. The denitration is essential for the preparation of the sol and is done in the ORNL-process by multiple solvent extraction of the $U(NO_3)_4$-solution with Amberlite LA-2 at various temperatures. The CNEN-extraction process yields a UO_2-sol with a too high acidity for internal gelation with a NO_3^- to uranium ratio of 1 to 1.5. In the KFA-process strong acids like HNO_3 or HCl are used for the peptisation. With a nitrate to uranium ratio of 0.2 an UO_2-sol is obtained with a sufficient low pH-value of 1.5-2. This sol can be used for the internal gelation without any difficulties. For the gelation at first a small amount of hexamethylenetetramine is stirred at 10°C into the concentrated sol, containing approximately 700 g uranium per liter and this mixture is added dropwise to paraffine oil at 95°C. The gel particles are washed in concentrated ammonia to remove any remaining nitrate or chloride ions, dried and then sintered at 1200°C in a reducing atmosphere. 90 % of all sintered kernels of each charge produced in the semitechnical-pilot-plant have shown deviation of the diameter of less than 10 %.

At this point it should be mentioned that the THTR with a power of 300 MWe has a daily consumption of only 7 kg of heavy metals.

Therefore, the demands of feed and breed material for a large power station can be satisfied by a relatively small plant. Fig. 4 shows UO_2 kernels after sintering with diameters of 8oo ± 5o/um and 16oo ± 1oo/um. The densities were determined to be up to 1o.8 g/cm^3, i.e. more than 98 % of the theoretical density. The high kernel density is shown in fig. 5a, where no porosity can be detected on the micrograph of a polished section. Porous kernels can be produced by a special heat treatment of the UO_2 gel particles (fig. 5b). It was already pointed out that this process is applicable for producing oxid kernels as well as carbid kernels. In the latter case, carbon black is dispersed in the sol by stirring before the gelation step. The carbon containing oxide kernels are then conversed to carbide by either melting in a graphite bed or by reaction sintering.

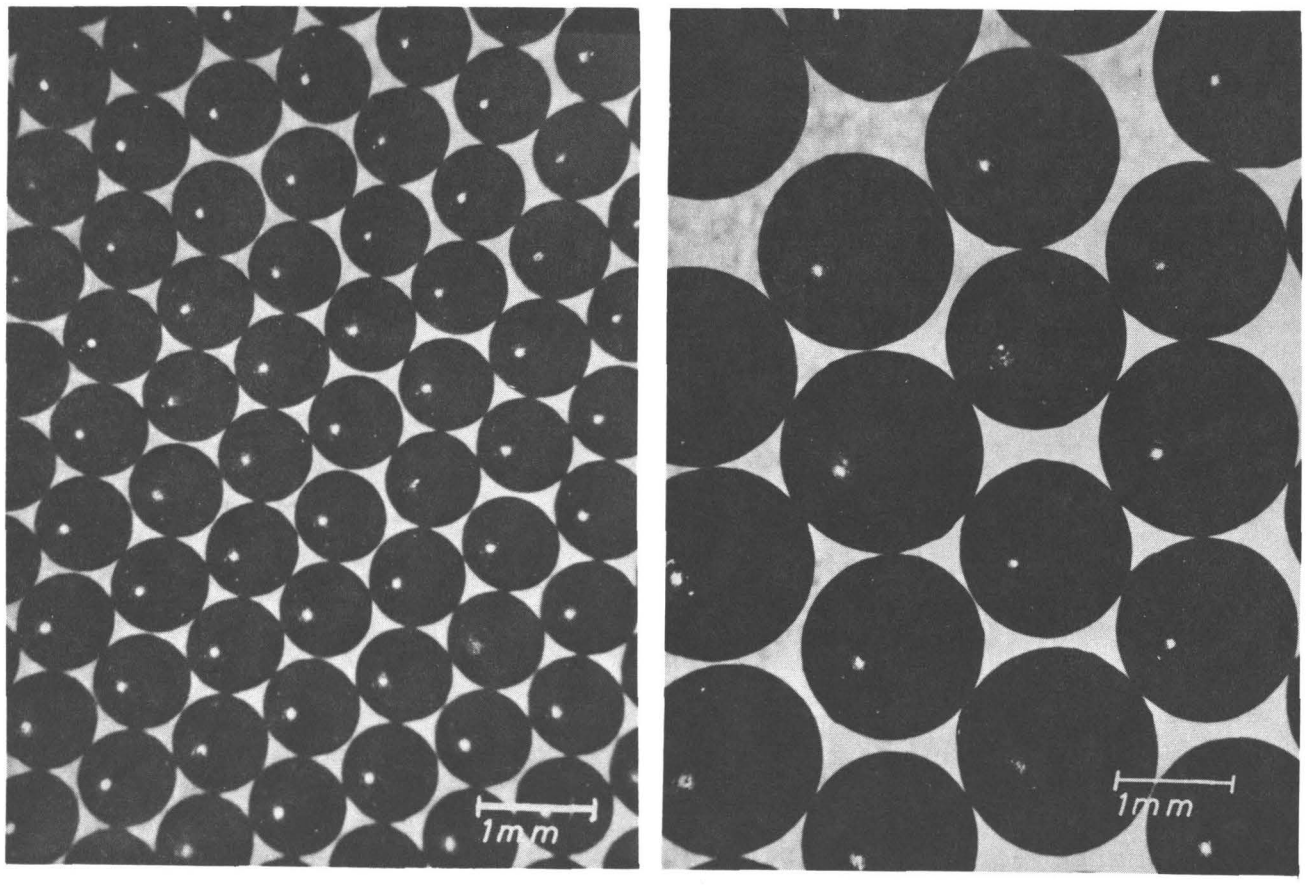


Fig. 4: UO_2-kernels with diameters of 8oo ± 5o/um and 16oo ± 1oo/um

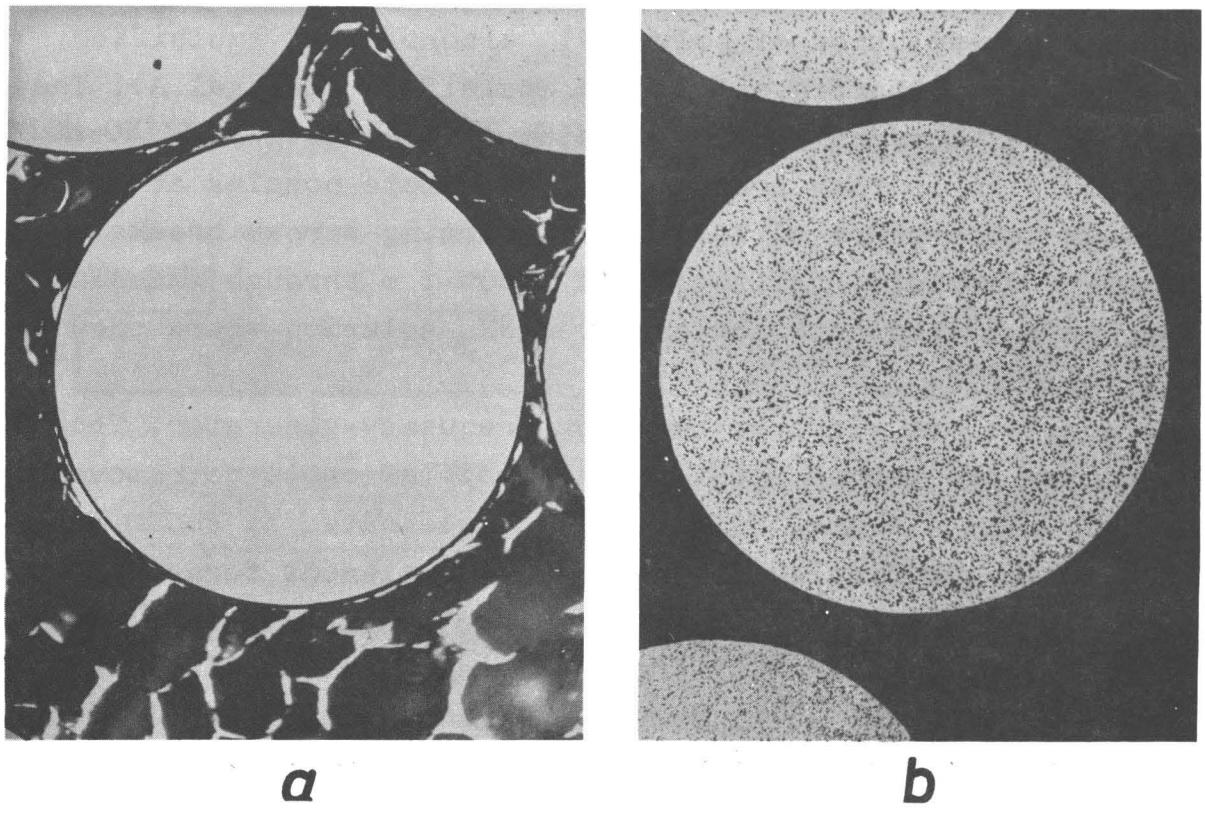


Fig. 5a,b: Non-etched polished micrographs of
a) a dense and
b) a porous UO_2-kernel
(KFA sol-gel process)

2.2 Uranium-VI-Processes

For preparing pure urania sols, the sol-gel processes start from U-IV-solutions therefore the normally available uranyl-nitrate solution has first to be reduced.
There were a number attempts to develope processes without this reduction step. In this connection, the NUKEM-emulsification[13]-process and the SNAM-process (Italy)[14] will described briefly. Both processes are running on a technical scale in plants with a throughput of 5-1o kg/day of heavy metal.

2.2.1 The NUKEM-Emulsification Process, SNAM-Process

The basis of both processes is the solidification of spherical droplets of pure $UO_2(NO_3)_2$- and/or $Th(NO_3)_4$- (eventually $Pu(NO_3)_4$-solutions) with certain organic additives in concentrated ammonia. In the NUKEM process, as an example for the

principle, the solution containing the heavy metals is mixed with an 8 %-solution of polyvinyl alcohole and emulsified after adding paraffin oil and an emulsifier (Etingal A). The heavy-metal content of the emulsion is 1oo-2oo g/l.
The emulsion is then pressed through simple nozzles at a maximum temperature of 2o°C. The outcoming stream breaks into discrete droplets, falling first about 1 m through gazeous ammonia and then into concentrated NH_3-solution where they are solidified.
The nozzles are vibrated by a low frequency-generator. The particles are washed with diluted propylalcohole to remove oil and ammonium nitrate, dried in air, calcinated at 8oo°C in a CO_2 stream and finally sintered in a continuous furnace at 15oo°C.
The principle of the SNAM-process is similar. Details were given first at the Gatlinburg Conference on Sol-Gel-Processes and Reactor Fuel Cycles (Gatlinburg, USA, May 197o). Up to this time, the process was only known in the patent literature. **Different organic additives, i.e. polysaccharides or** cellulose-derivates and tetrahydrofurfurylalcohole **are used.**
The disadvantage of these processes is that no kernels of high density can be produced. The maximum attainable density of sintered kernels is approximately 95 % of the theoretical density. Furthermore, it is difficult to produce with this processes small kernels with diameters in the range of 2oo-3oo µm as required for "feed cycles".

.2.2 The KFA-H-Process[12] and the KEMA-Process[15]

On the occasion of the Gatlinburg Sol-Gel Conference KEMA and KFA have reported for the first time two new sol-gel processes for the direct processing of uranium-VI solutions to produce spherical UO_2-kernels.
Both processes, developed independently, are based upon the internal gelation of a $UO_2(NO_3)_2$ solution of high uranium concentration in the presence of urea. In fig. 6 the flow-**sheets** for both processes are compared. It is advantageous that in these U-VI-proceeses some steps can be omitted which simplifies the production of kernels considerably.

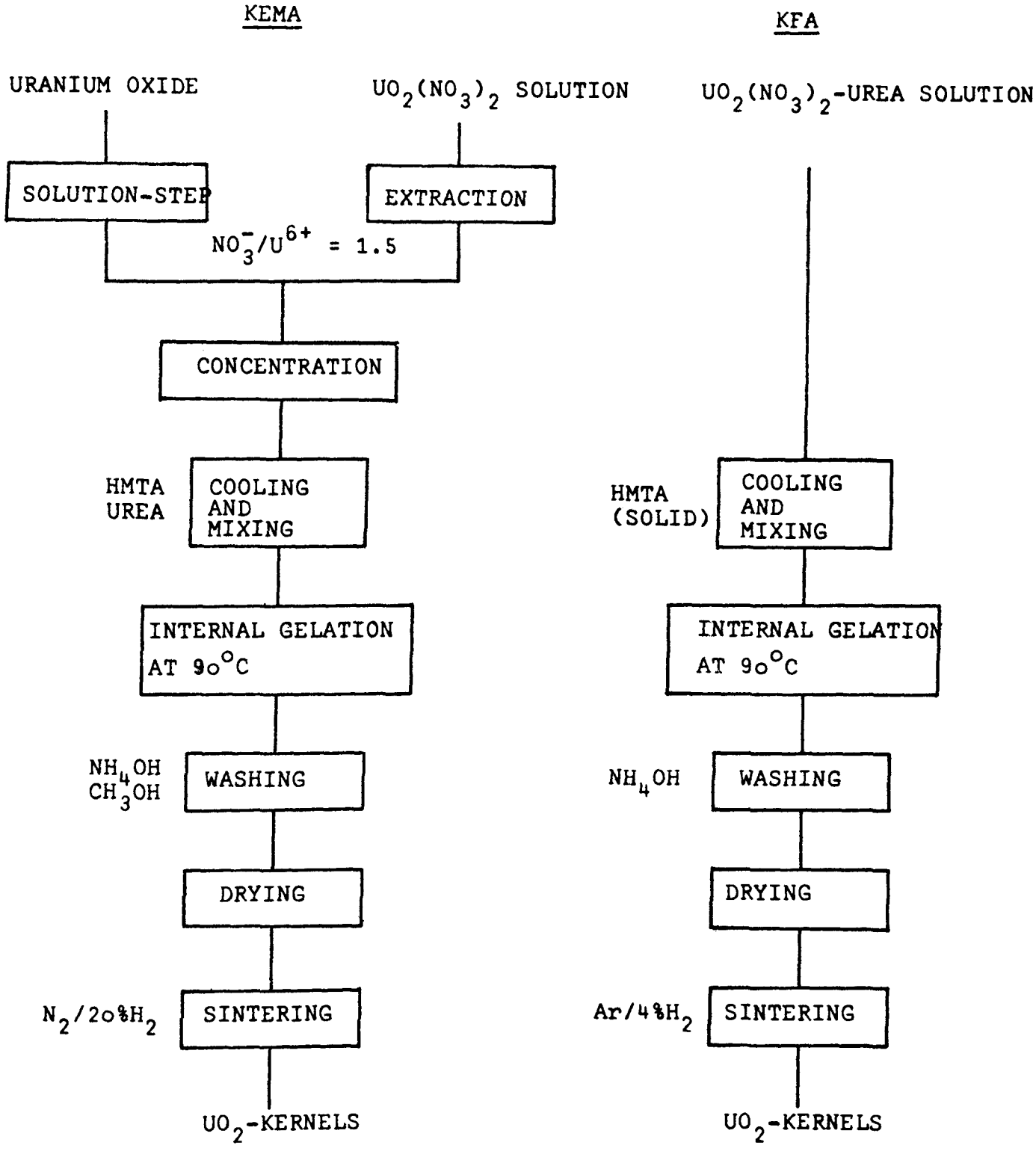


Fig. 6: Flow sheets of the KFA- and KEMA-U(VI)-Processes

In the KFA-H-Process the necessary high uranium concentration (about 3 molar) is achieved by simultaneous dissolution of UO_2-$(NO_3)_2$ and urea, the gelation agent hexamethylentetramine is then added in solid form. By dropping the solution into a bath of paraffin oil at 95°C- the droplets are solidified by "internal gelation" (formation of amorphous UO_3). After washing and drying the particles are sintered in a reducing argon hydrogen atmosphere forming high density pore-free UO_2-kernels.
The difference between the KEMA-process and the KFA-H-process is that KEMA starts from a substoichiometric U(VI)-solution which has to be concentrated by evaporation. To this concentrated solution a solution of urea and hexamethylentetramine is added.
Due to the simplicity of these processes and the fact that oxide or carbide kernels of any desired size can be produced, it could gain a great interest for the production of fuel kernels in the future. At KFA this process is tested in a kg-scale pilot plant.
During the last years by various research centers and industrial firms a number of processes for the production of spherical fuel kernels have been developed, which will not be mentioned in this report because they either are in principle similar to the already described processes or are from the present point of view, of no importance for further technical development.

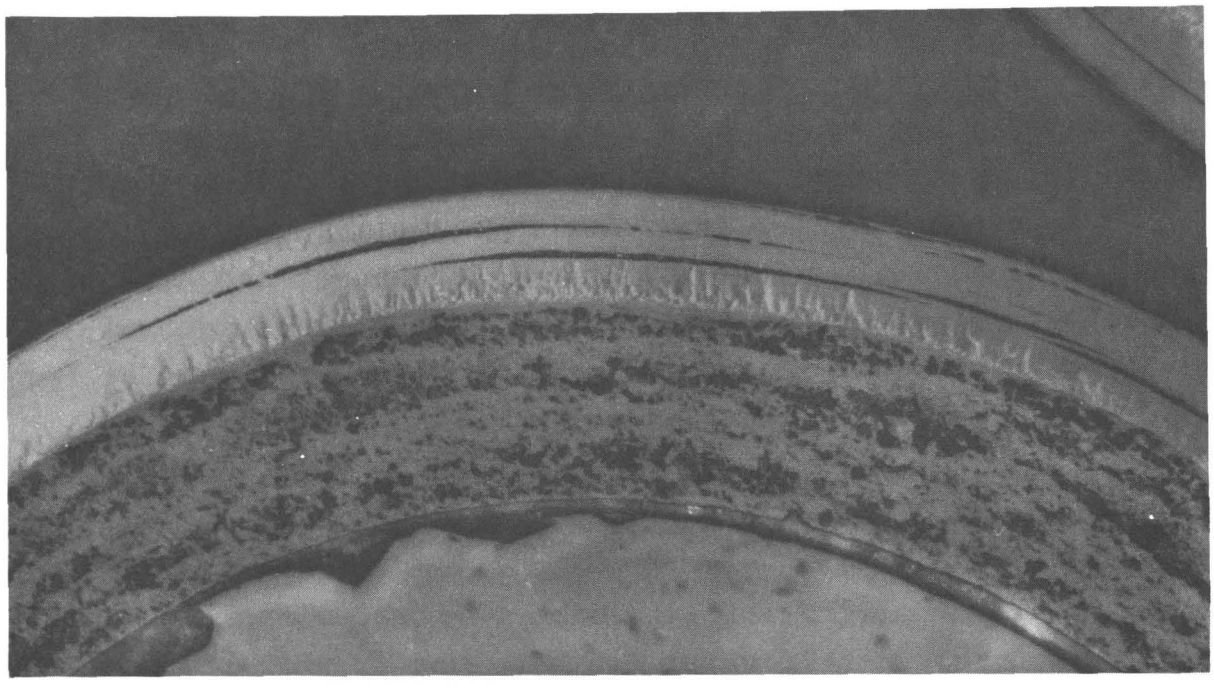
3. Coating of fuel kernels with pyrocarbon or silicon carbide

As mentioned the spherical oxide or carbide fuel kernels are usually coated with layers of pyrocarbon or additional layers of carbides (for example with silicon carbide). The relations between coating structure and irradiation stability respectively permeability for solid fission products are not understood to a great extent. The investigation at KFA are therefore concerned with the following topics: the production of irradiation-samples with defined coating structures and definite properties, the determination of the change of the physical and mechanical properties of the coating material by irradiation and the investigation of the

diffusion behaviour of the heavy metals uranium and thorium and of some fission products.
Depending on the concentration of different hydrocarbones or silanes and the temperature of decomposition (pyrolysis), pyrocarbon or silicon-carbide coatings with different structures and densities can be obtained resulting, in different physical and mechanical behaviour. The kernels are coated with one or more layers of PyC or in some cases an additional layer of SiC in fluidized beds of various sizes. In the KFA fluidized beds with diameters of 1, 2 and 3 inches are used. These fluidized beds consist of a vertical double-contained water-cooled, cylindrical stainless steel pipe. In the centre of this pipe a graphite resistence heating system is mounted which contains the graphit-bed tube with the kernels to be coated. Carrier gas is usually Argon to which either methane, acetylene or propene is added, depending on the desired coating structure and density. The coating temperature is in the range of 1200 to 2000°C and depends on the nature of the desired coatings.
There are several publications on the coating process and on investigations of the properties of PyC. They are compiled in a literature survey[16].

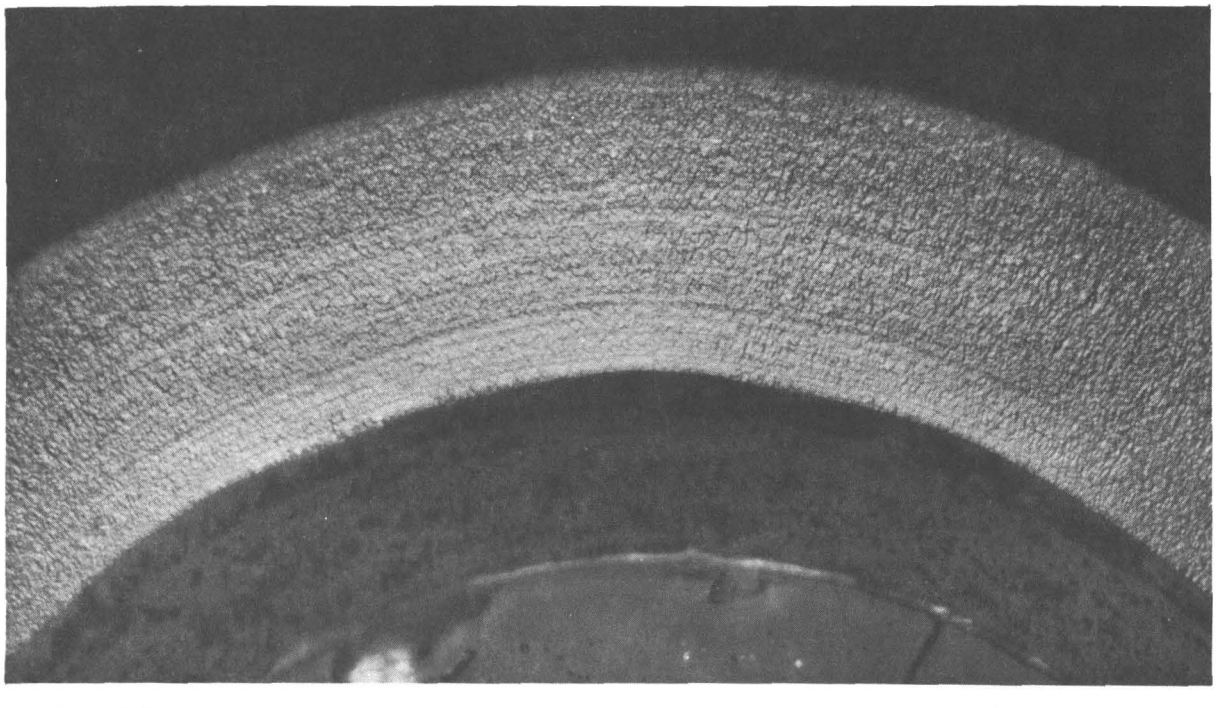
3.1 Pyrocarbon from the Methane-Pyrolysis

Depending upon the pyrolysis-temperature and the methane concentration three different areas of pyrocarbon structure can be distinguished: 1. coatings with a laminar, 2. coatings with an isotropic and 3. coatings with granular resp. columnar structure. In fig. 7a an outer PyC-layer is shown wich was attained at 1300°C with a low methane concentration (5 Vol.%). In fig. 7b a fine-granular structure is shown, which was also obtained at 1300°C but at a higher concentration of methane (22 Vol.%). In fig. 8 three different structures can be distinguished: the inner porous layer was produced by decomposition of acetylene; the next layer was deposited from 22 Vol.% methane at 1500°C to 1900°C and the outer layer has a columnar structure which has been formed at high pyrolysis temperatures and low methane concentration.



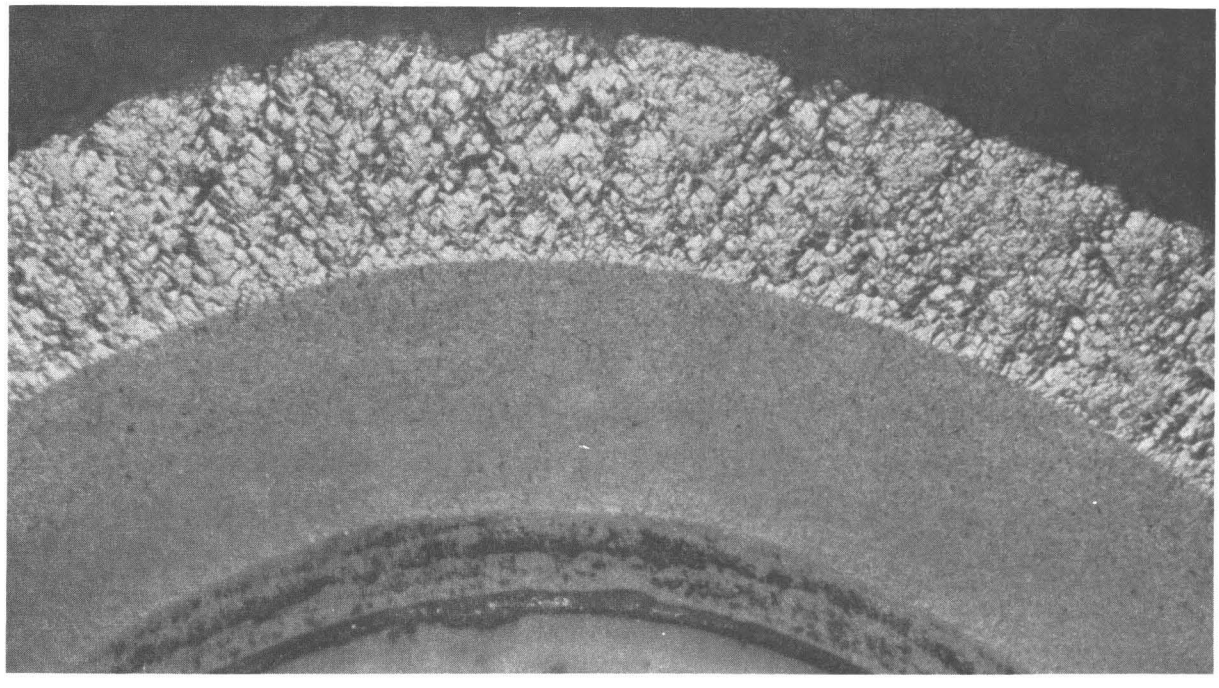
pol. light 5oo x

Fig. 7a: Micrograph of a polished section of a coated particle with a laminar PyC-structure (MAUTO 67)
Structure: laminar; ρ_{PyC} = 1,62 g/cm^3;
Conditions of deposition: 13oo°C, 5 Vol-% CH_4



pol. light 5oo x

Fig. 7b: Micrograph of a polished section of a coated particle with a fine-granular-laminar PyC-structure (MAUTO 68)
Structure: fine-granular-laminar; ρ_{PyC} = 1,96 g/cm^3;
Conditions of deposition: 13oo°C, 22 Vol-% CH_4



pol. light 5oo x

Fig. 8: Micrograph of a polished section of a coated particle with an isotropic and columnar structure (MAUTO 79)

Structure: 1st layer: porous; ρ_{PyC} 1 g/cm^3
2nd layer: isotropic; ρ_{PyC} = 1,7 g/cm^3
3rd layer: columnar; ρ_{PyC} = 2,o9 g/cm^3

Deposition conditions:
porous layer: 15oo°C; 5o Vol-% C_2H_2
isotropic layer: 15oo°C-19oo°C; 22 Vol-% CH_4
columnar layer: 19oo°C; 5 Vol-% CH_4

Today isotropic coatings are known to have the best irradiation stability. For HT-reactors the demand is therefore to use only coated particles with coatings as isotrop as possible.
The "orientation-anisotropy" of the crystallites in the pyrocarbon-layers is determined by the measurement of the so-called BACON-Anisotropy- Factor (BAF). Isotopic pyrocarbon layers of coated particles should have BAF-values between 1.o and 1.o5 whereas the best densities are between 1.75 and 1.95 g.cm^{-3} as

proved in irradiation experiments with high fast neutron doses and high temperatures.
PyC-layers with low densities shrink during irradiation, PyC with densities greater than 2 $g.cm^{-3}$ a decrease of the density occurs.
In fig. 9 and 1o the irradiation induced change of PyC density is plotted as a function of fast neutron dose from results of fast neutron irradiation experiments (DN I and DN II) performed at the Dounreay Fast Reactor (DFR)[17]. At fast doses of 1.7 resp. 1.8-1o$^{22}n.cm^{-2}$ (E $\geq$ o.1 MeV) the changes of the density may be greater than 2o %, depending on the initial density.
It must be mentioned that these high experimental doses are 2.5 to 3 times higher than the specified values for the THTR. Furthermore these measurements have been obtained not on PyC-coated particles but on PyC-coated graphite discs which are coated together with particles in each coating run in the fluidized beds.
The radiation induced relative density change of PyC also depends on the irradiation temperature and the integrated dose of fast neutrons. This is shown in fig. 1o with the initial density as parameter. The irradiation temperature was 135o $\pm$ 1oo°C.
Some results of a coating study, performed in an 1 inch fluidized bed are summarized in fig. 11. The influence of deposition temperature and CH_4-concentration on the PyC structure, density and BACON-Anisotropy-Factor is apparent. Using these Data, isotropic PyC with the required properties can be obtained in an 1-inch bed by pyrolysis of methane at temperatures between 18oo and 2ooo°C and CH_4-concentrations between 2o and 25 Vol.%.
At higher CH_4 concentrations a considerable deposition of carbon black occurs and therefore a decrease of the PyC density. In bigger fluidized beds the results are only slightly different.
At deposition-temperatures higher than 18oo°C the diffusion of uranium and thorium into the PyC layers cannot be prevented completely as the concentration profile of uranium in the outer PyC-ayer of a coated particle indicates (fig. 12).

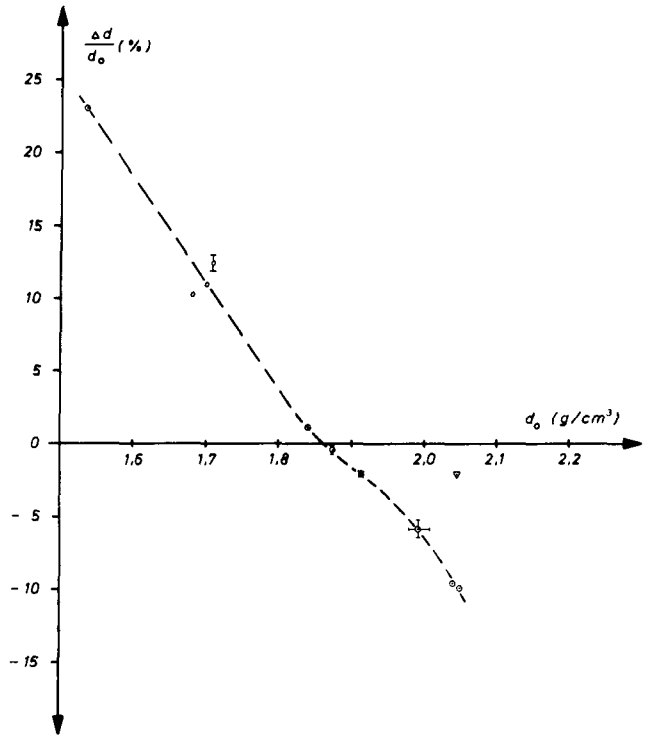


Fig.9: Relative density changes of PyC by fast neutrons as a function of the initial density.
Irradiation experiment DN II; fast neutron dose $1.7 \cdot 10^{22}$ n.cm^{-2} (E ⩾ o,1 MeV); Irradiation temperature: 135o ± 1oo°C

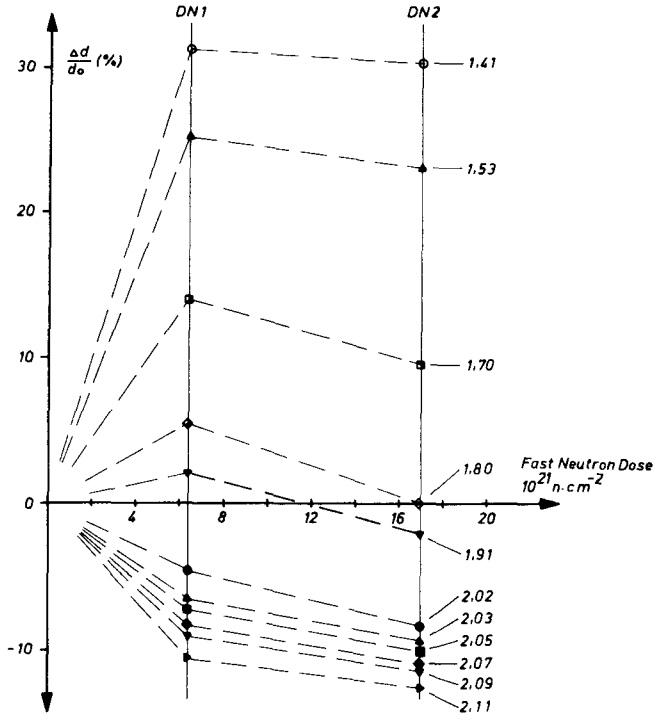


Fig. 1o: Relative density changes of PyC with different initial densities as a function of the fast neutron dose (E ⩾ o,1 MeV);
Irradiation experiments DN I and DN II;
Irradiation Temperature: 135o ± 1oo°C

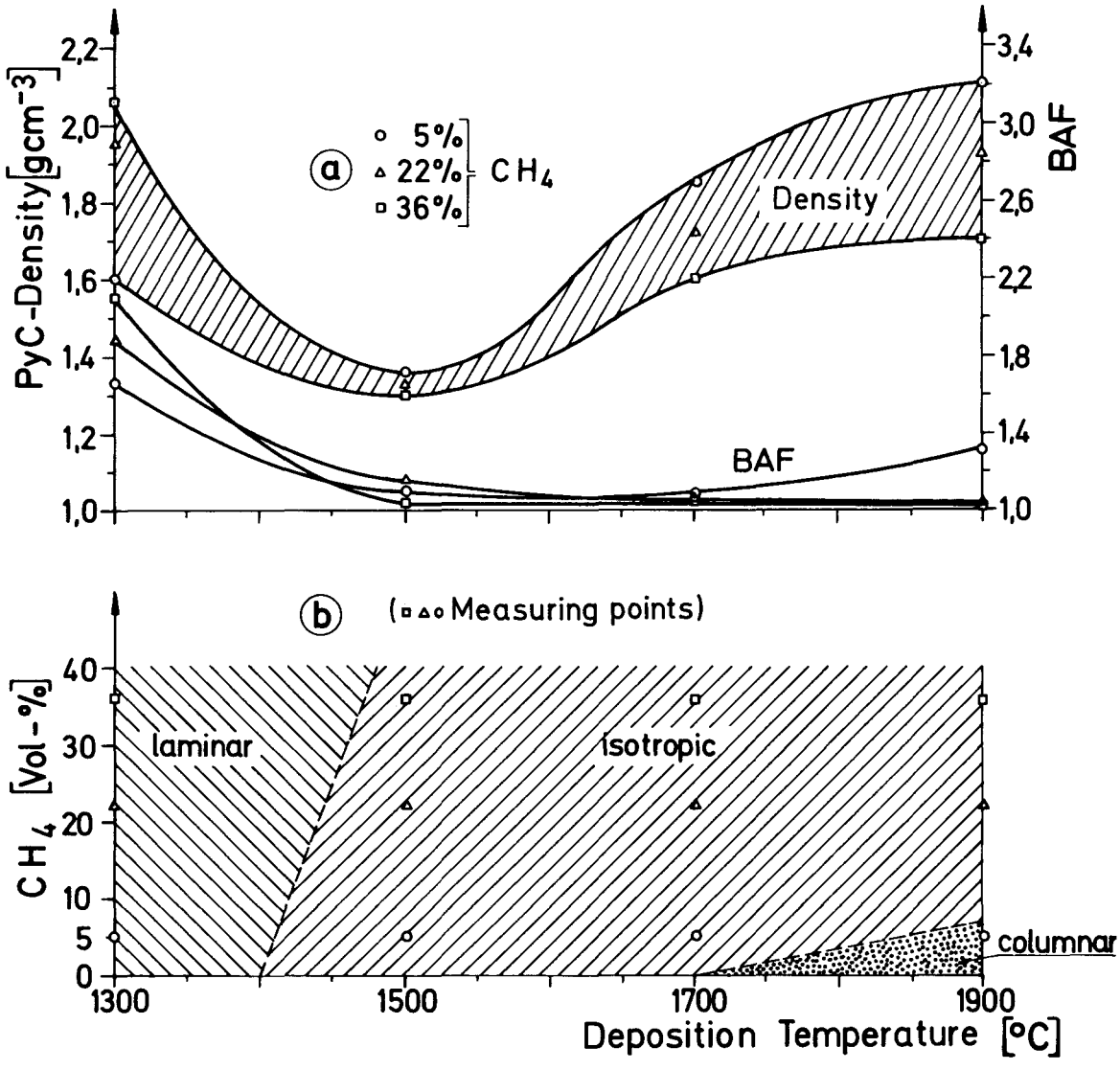


Fig. 11: Correlation between deposition temperature, methane-concentration and PyC density resp. BAF (a) and the PyC structure (b) (1 inch fluidized bed).

A very sensitive analytical method for U-determination and a mechanical grinding procedure have been developed to remove the PyC coating in steps of about 1o µm thickness and to determine the U-content in these samples[18]. In the Institut für Reaktorentwicklung at KFA Jülich, a wet-chemical abrasion method was developed, which is particularly suited for the determination of fission product profiles in the PyC coatings of irradiated coated particles[19].

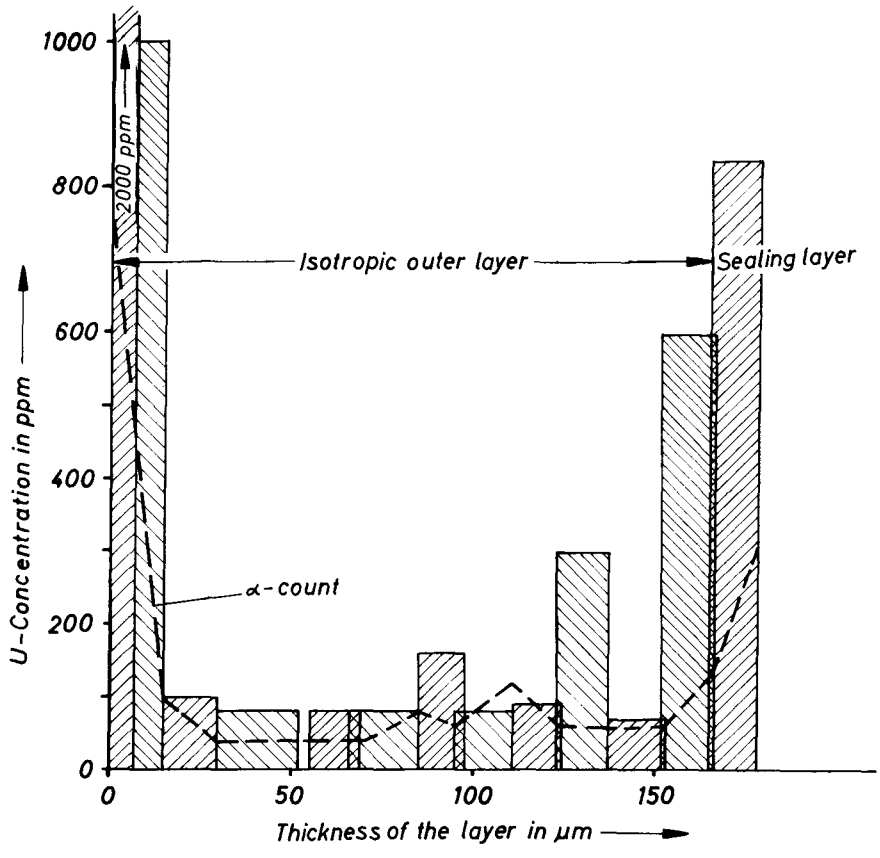


Fig. 12: Profile of uranium-concentration in the outer PyC-layer of an UO_2-fuel coated particle (average of 1oo particles)

The investigation of uranium and thorium transport through PyC is the subject of a KFA-Jülich/SGAE-Seibersdorf joint program. The measurements are performed either on PyC coated graphite discs (SGAE) or on coated particles (KFA). The main object is the dependence of the heavy metal transport on the PyC structure.

Since contamination of the PyC-coating by heavy metals during the coating process causes a considerable increase of the fission product concentration in the power reactor cooling gas it should be prevented. **One way towards** this aim is to keep the deposition temperature as low as possible. During the last years other gases than methane have been used for the pyrolysis. From independent work at ORNL[2o], NUKEM[21] and KFA[21,22] and recent irradiation results propene seems to be a particularly well suited deposition gas.

3.2 Pyrocarbon from propene pyrolysis

In the following section some results obtained at KFA-Jülich on the propene pyrolysis are discussed. In fig. 13 the correlation between deposition-temperature, propene concentration and PyC-density resp. Bacon Anisotropy Factor (BAF) and the PyC-structure are given as an example. The figure shows that depending on the bed size either columnar or dense isotropic or carbon-black containing isotropic or porous PyC-structures are attainable.

Contrary to the methane pyrolysis, by the propene pyrolysis isotropic PyC-layers can be produced at temperatures as low as 1200 to 1350°C.

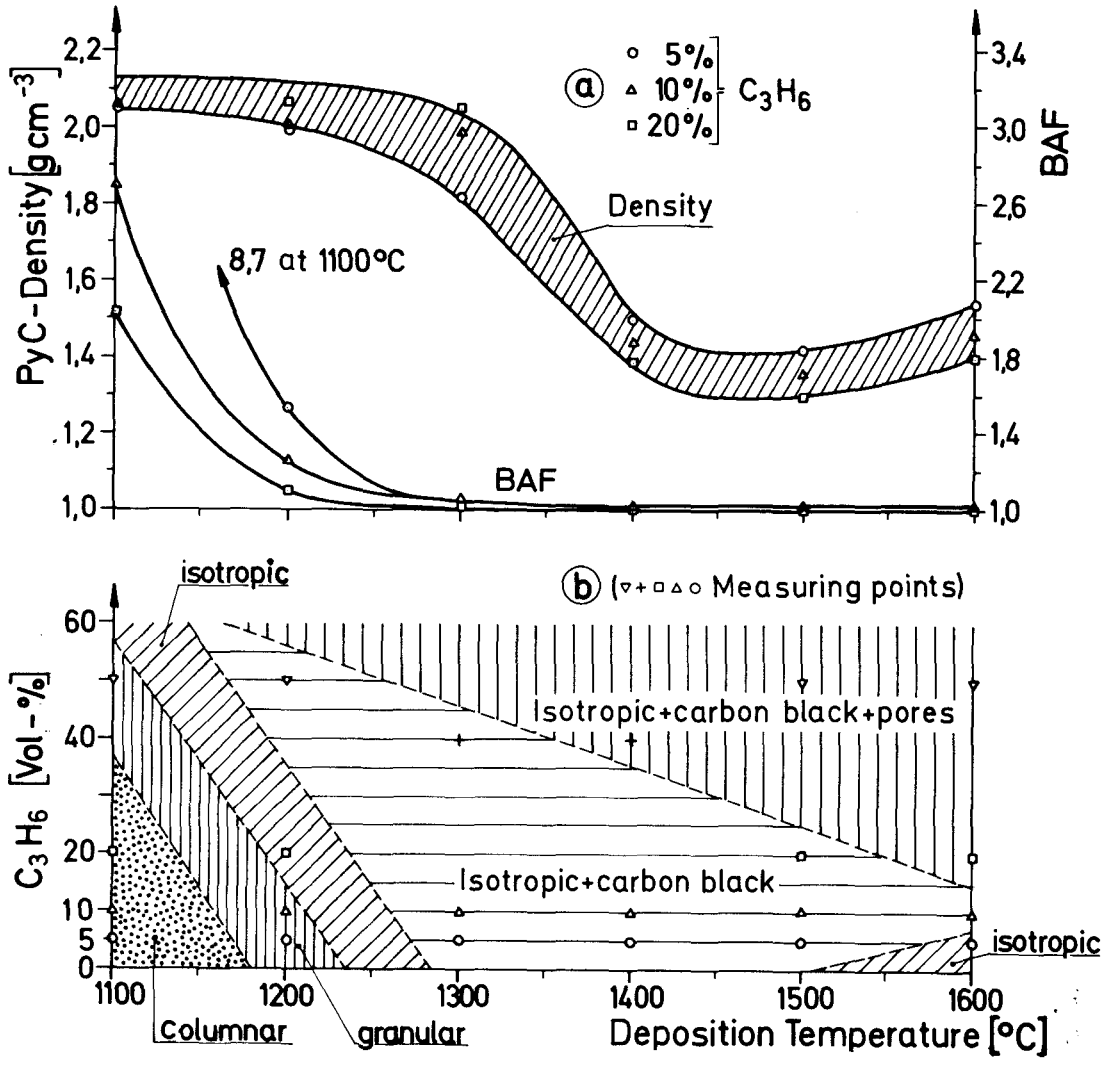


Fig. 13: Correlation between deposition temperature, propene concentration and PyC-density resp. BAF(a) and PyC-structure (b). (1 inch fluidized bed.)

The apparent crystallite size L_c of this PyC is between 2o and 6o Å and is a function of the C_3H_6 concentration and of the fluidized bed geometry. As already demonstrated temperatures between 18oo° and 2ooo°C are required to deposite PyC of comparable density and structure from methane. The L_c values are ranging in this case between 7o and 16o Å. Recently new results of irradiation experiments concerning PyC which was deposited by the pyrolysis of propene have been published by American authors[23]. Fig. 14 shows the change in density of PyC obtained by the pyrolysis of propene as a function of the integrated fast neutron dose. The left figure shows the already known change of density of CH_4-deposited PyC as a function of integrated fast neutron dose. As in the KFA-Dounreay irradiation a final density of 1.8 to 1.9 $g.cm^{-3}$ is obtained at a fast dose of $1.1o^{22}$ $n.cm^{-2}$ independent on the initial density.

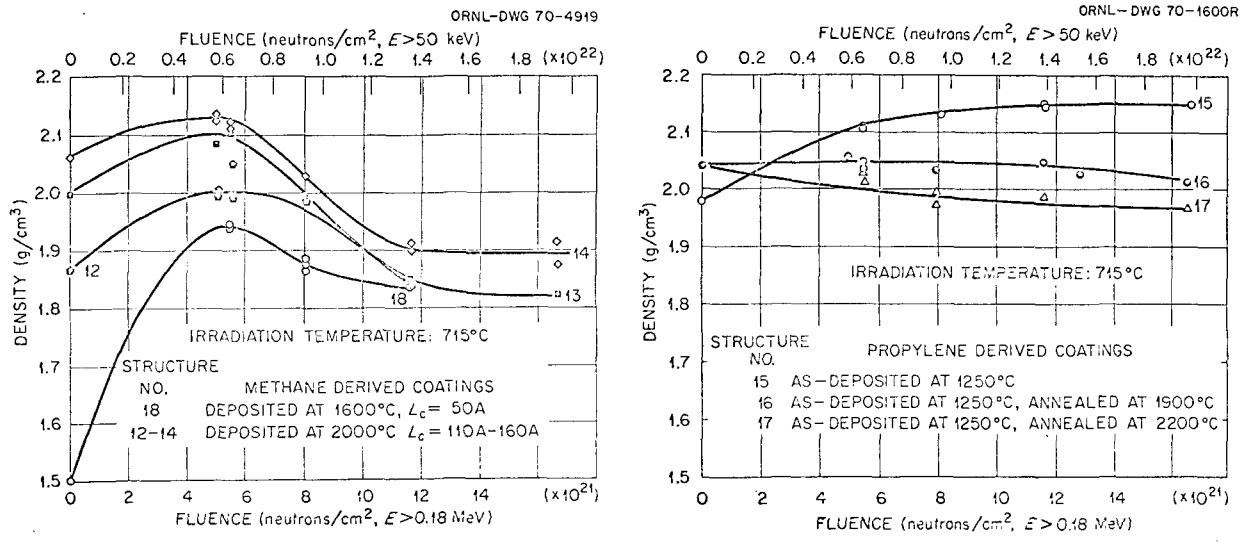


Fig. 14: Density change of PyC as a function of the integrated fast neutron dose (E ⩾ o,18 MeV)[23]

In the figure on the right side radiation induced changes of the density of propene-deposited PyC is shown as a function of the integrated fast neutron dose. It is obvious that these density changes are very small, especially when the propene-deposited PyC was tempered at 19oo to 22oo°C before irradiation. It should, however, be mentioned, that the irradiation temperature was only 715°C. The Institut für Reaktorwerkstoffe of KFA at Jülich has very recently performed an irradiation experiment in the High Flux Isotopic Reactor at Oak Ridge, where coated particles with propene- and methane-deposited PyC have been

irradiated to an integrated fast neutron dose of $6.1o^{21} n/cm^2$ at 8oo°C. The particles with propene-deposited coatings showed a better irradiation behaviour than the particles with methane-deposited PyC. But a final judgement can only be given if more irradiation results are available with a systematic variation of the conditions of PyC-deposition and irradiation parameters.

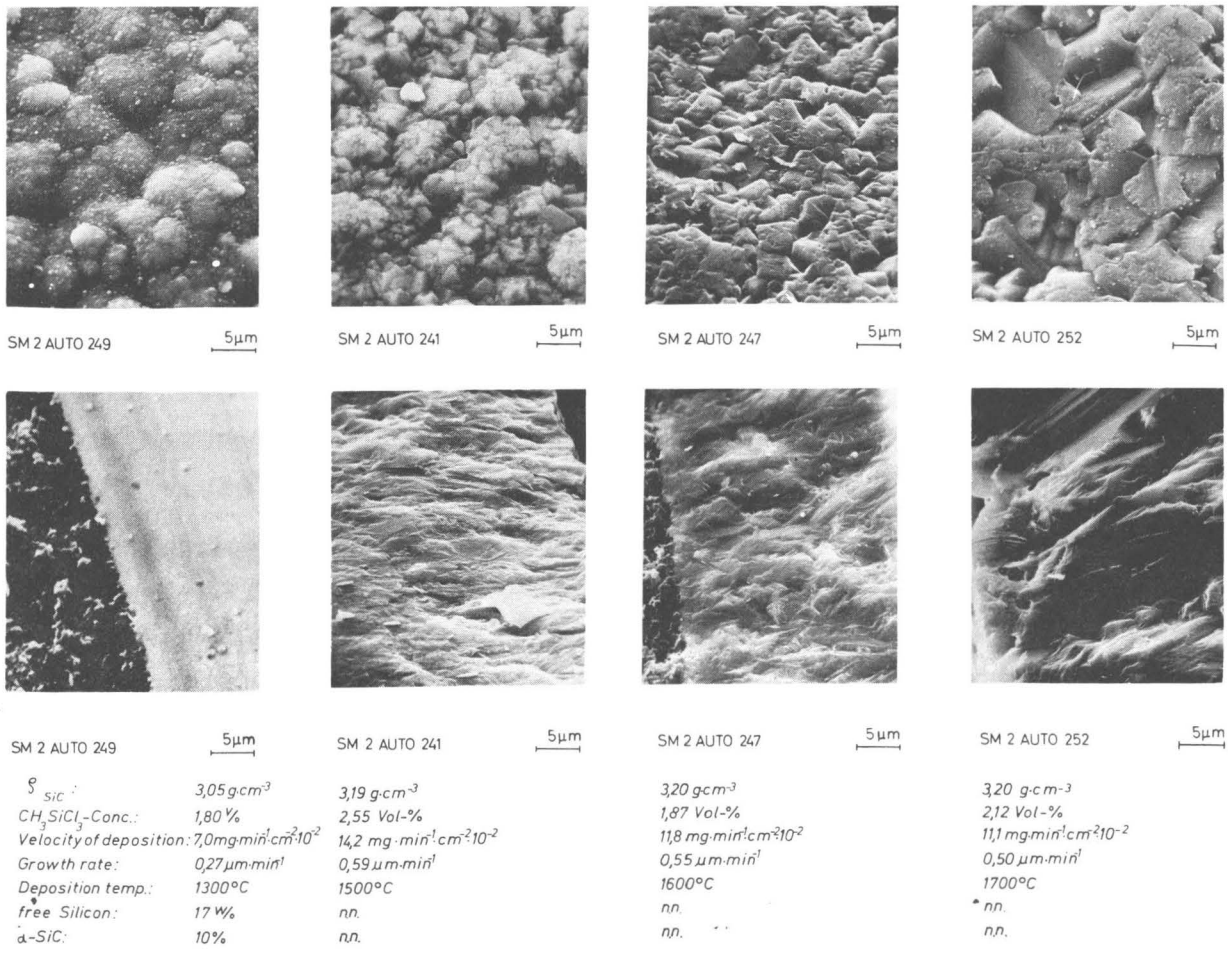
3.3 Silicon-carbide coatings

The demand for a high fission product retention is not fulfilled by PyC coatings for some fission products such as Sr, Ba and Cs. An additional barrier of silicon-carbide has given considerable advantages. The release of these fission products from particles with a silicon-carbide interlayer are up to three orders of magnitude lower. SiC easily can be produced by thermal decomposition of methylchlorsilanes.

Investigations performed by the DRAGON Project[24] have shown that silicon-carbides of quite different properties can be produced in fluidzed beds, depending on the silane and the deposition temperature. Fig. 15 shows electron micro photographs of pyrolytically deposited SiC on coated fuel particles. The upper pictures show the surface of the silicon carbide layers. The deposition temperatures were varied (12oo, 15oo, 16oo and 17oo°C) and the CH_3SiCl_3 concentration was between 1,8 and 2,55 Vol.%. The micrographs indicate a high density of the SiC deposited at a low temperature (3.o5 $g.cm^{-3}$ at 132o°C). The deposite is mainly α-SiC with free silicium. The surface is "bubble"-like with small spheres inlayed. First signs of crystalline structures appear at 15oo°C, but still the bubbles remain. At 16oo°C the structure is crystalline and at 17oo°C the crystallites are even larger, forming a dense, interconnected structure. The lower pictures show the electron scan-micrographs of the surfaces of fractures. Whereas at 13oo°C various layers could be identified in the SiC-structures, at a higher temperatures clear fractured coherent surfaces of SiC crystallites can be observed.

It can be assumed, that SiC with a density as high as possible offers a favourable fission-product retention behaviour and an optimal irradiation stability. Such SiC coatings can be produced

in fluidized beds without difficulties at temperatures between 1550° and 1700°C. In Germany so far no irradiation results for SiC have been attained. Work concerning retention of solid fission products was recently started in the Federal Republic of Germany.



ρ_{SiC}:	3,05 g·cm^{-3}	3,19 g·cm^{-3}	3,20 g·cm^{-3}	3,20 g·cm^{-3}
CH_3SiCl_3-Conc.:	1,80 %	2,55 Vol-%	1,87 Vol-%	2,12 Vol-%
Velocity of deposition:	7,0 mg·min^{-1}·cm^{-2}·10^{-2}	14,2 mg·min^{-1}·cm^{-2}·10^{-2}	11,8 mg·min^{-1}·cm^{-2}·10^{-2}	11,1 mg·min^{-1}·cm^{-2}·10^{-2}
Growth rate:	0,27 µm·min^{-1}	0,59 µm·min^{-1}	0,55 µm·min^{-1}	0,50 µm·min^{-1}
Deposition temp.:	1300°C	1500°C	1600°C	1700°C
free Silicon:	17 %	nn.	nn.	nn.
α-SiC:	10%	nn.	nn.	nn.

Fig. 15: Stereoscan micrographs of pyrolytical deposited SiC on coated fuel particles.
Upper pictures: surface view
Lower pictures: view of a fractured surface

4. Prismatic particle boddy

It has already been mentioned, that the coated particles in either the spherical fuel elements of the THTR or in the prismatical fuel elements (rods or blocks) are present in the form of compacts. Spherical moulded fuel elements for the THTR have been fabricated by NUKEM by a mouldening process specially developed within the frame of THTR program[13].

The raw material for the matrix is a mixture of natural graphite, electro-graphite and phenol resin as a binder. This blend is mixed with the coated particles and quasi-isostatically pressed in a rubber mould to form a spherical ball.
This particle-bearing sphere is in a similar pressing step enclosed in a thinner particle-free outer layer of pure graphite. The binder is carbonized at 800°C followed by a temperature treatment at 1800°C which considerably improves the mechanical strength and the heat conductivity.
This type of fuel element has been operated with good success in the AVR-power station and in THTR specification tests. In the frame of the fuel and materials development work for the KWSH (Kernkraftwerk Schleswig-Holstein), which will be operated with prismatic fuel elements, investigations on prismatic fuel compacts have been commenced in the Federal Republic of Germany. NUKEM has produced the first compacts in close collaboration with KFA and the first irradiation tests are under way.
In a compact, the coated particles are embedded - as in the moulded sphere - in a matrix consisting of a filler material (graphite powder) amd a binder (phenol resin). There is a distinction between compacts and bondings and from the comparison of the flow schemes of both processes (fig. 16) it can be seen that in a compact the particles and the matrix are moulded under pressure whereas in bondings they are merely sticked together. The heat treatments at 800°C (carbonisation) and 1800°C are similar as described for the spherical elements. From irradiation experiments it is known, that at high temperature and in a high flux of fast neutrons graphite **bodies shrink** due to a radiation induced graphitisation of the binder. The same effect can be observed in compacts and bondings.
Spherical fuel elements of the hollow sphere type which contain the coated particles in 4 to 5 layers bonded onto the inner surface of a hollow graphite sphere have shown failures caused by radiation induced binder shrinkage. In fig. 17 an example of such radiation induced failure is shown. After an irradiation period of 250 days, an integrated fast neutron dose of $1.5.10^{21} n.cm^{-2}$, ($E > 0{,}1$ MeV) and a burnup of max. 9 % fima, up to 3 % of the coated particles failed, due to binder-shrinkage.

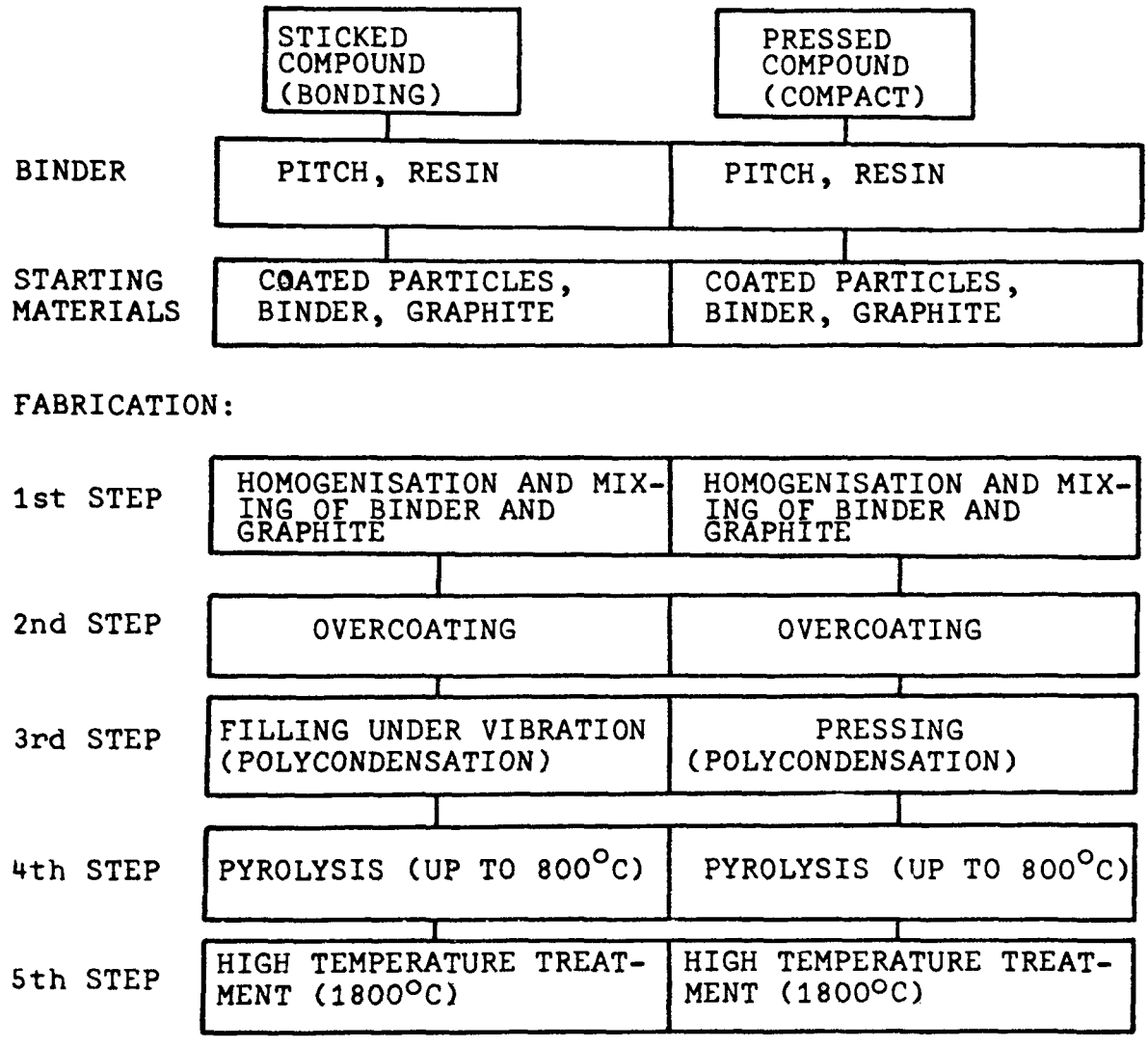


Fig. 16: Flow sheet for the fabrication of fuel compounds (schematically).

To obtain a better knowledge about the phenomenon of binder shrinkage, several compacts and bondings with two different phenol resin binders and graphites in different compositions are being prepared or already in an irradiation test in the DFR. First results from irradiation tests in the DFR at Dounreay and in the R2 at Studsvik (Sweden) gave important references for the planned experiments.

Apart from this irradiation program experiments are performed to optimise the conditions of carbonisation during the fabrication of compacts. The behaviour during pyrolysis is investigated with different binders and mixtures of binder and filler. The aim is to find binders with no or only neglectable radiation induced changes.

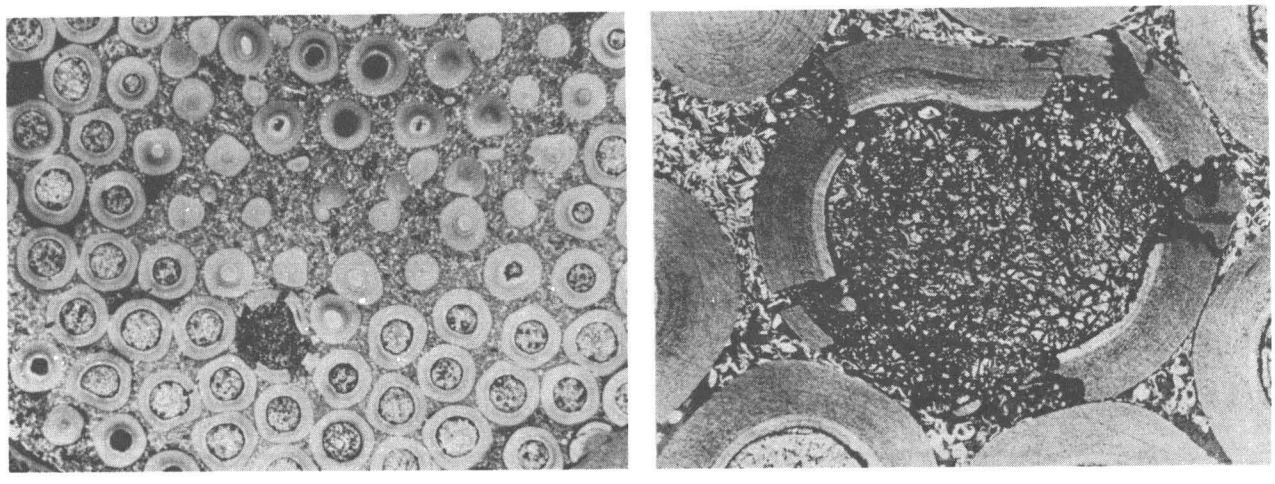


Fig. 17: Part of a section of a spherical fuel element of the hollow sphere-design. Irradiation damages caused by neutron induced binder-shrinkage.
HTR-irradiation experiment TD-2, fast neutron dose 1,5 . 10^{21} n.cm^{-2} (E > o,1 MeV).
Irradiation time 25o days; burn-up: 9 % fima.

5. Irradiation of coated particles

The HTR material development work in the field of coated particles is mainly performed in a joint program by NUKEM and KFA, whereby the irradiation experiments are coordinated and the post irradiation examinations are carried out by KFA. In fig. 18 the running irradiation experiments with coated particles are summarized (state of 3o.6.197o). The type of irradiated sample is plotted against burn-up and fast neutron dose for all experiments under irradiation, neglecting those already finished or in preparation. Fig. 18a shows the same data for successfully terminated irradiation experiments (state of 1. 1. 1971).

Before entering into details, some general remarks about irradiation experiments will be made. There are two distinct types of tests: Performance tests of reference particles for HT-power reactors (AVR, THTR, KWSH and in the future for HHT) and tests for investigations on the irradiation behaviour of model particles.

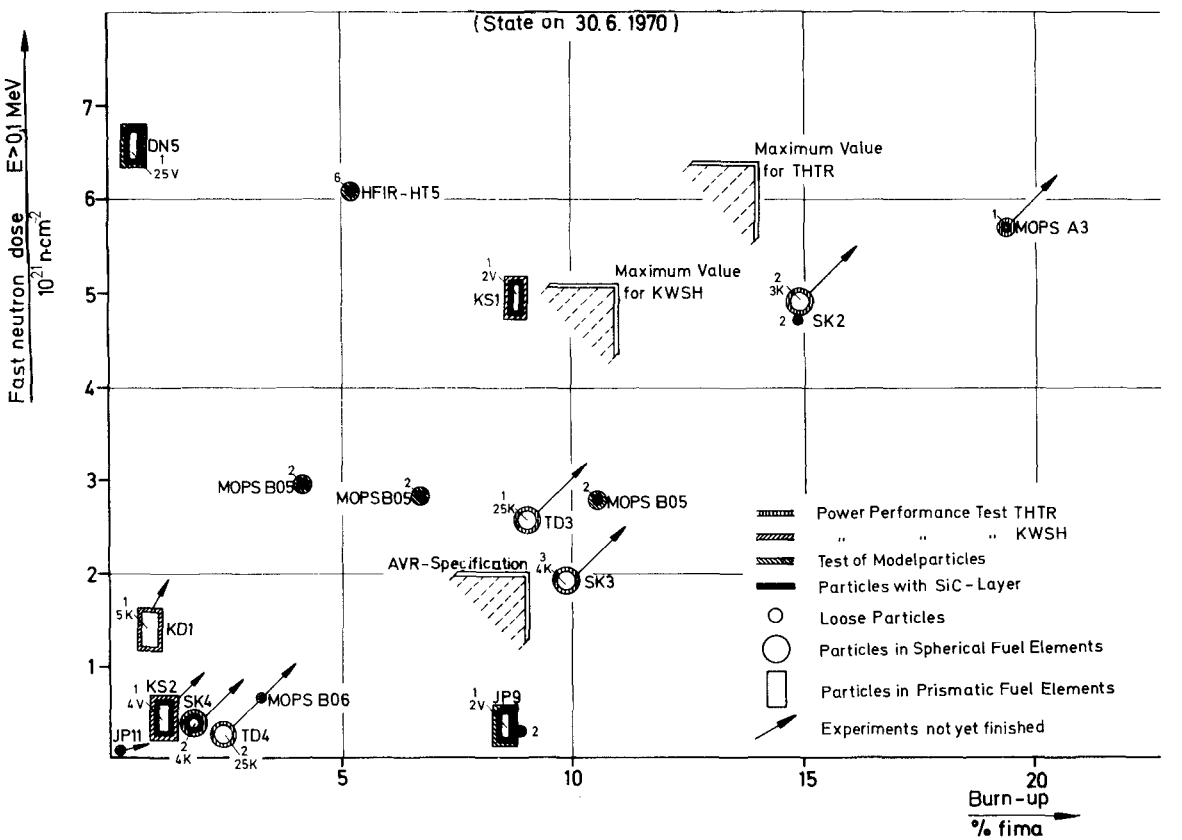


Fig. 18: Irradiation experiments presently performed with coated particles with achieved fast neutron dose and burn-up. (State of 3o. 6. 197o)

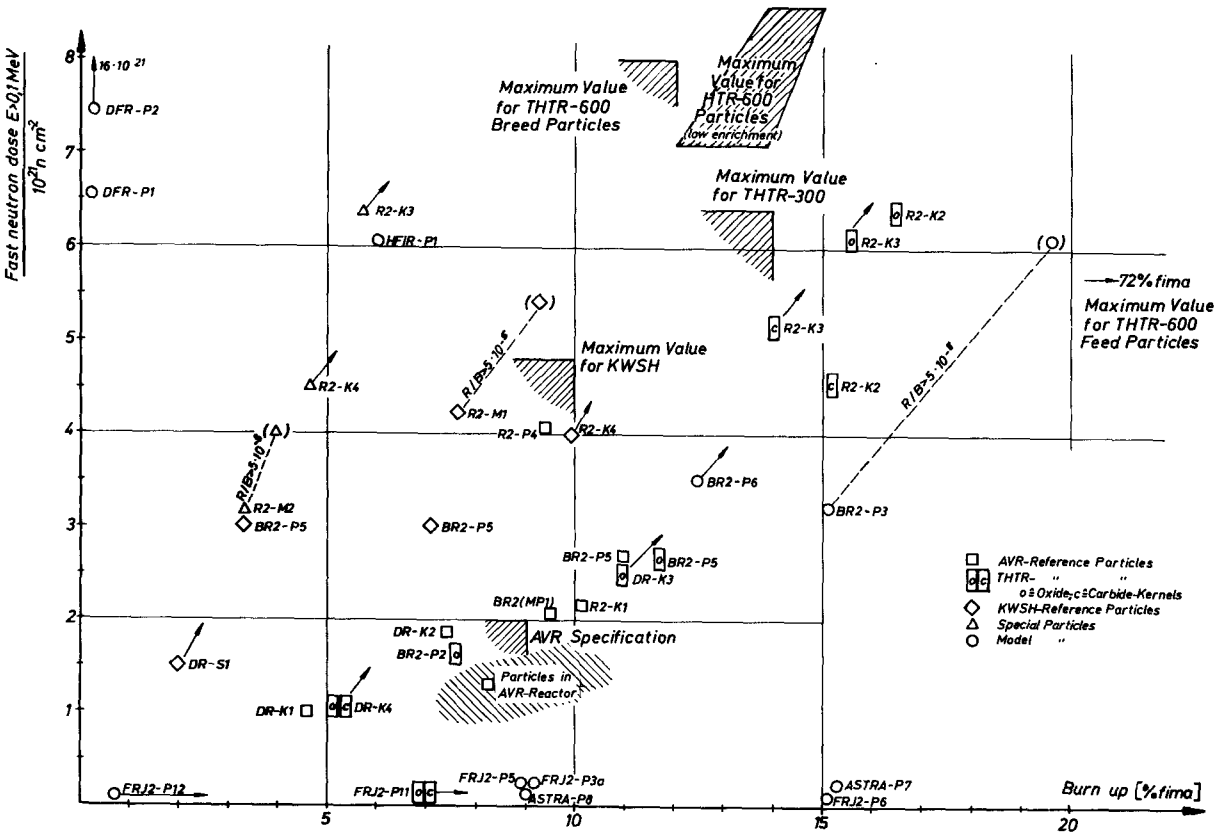


Fig. 18a: Successful irradiation test (R/B-Xe-133 < $5.1o^{-5}$) on coated particles (state of 1.1.1971)

5.1 The irradiation of HT-Reactor Reference Particles

In table 3 the **fuel data for the HTR Reactors planned or under construction are summarized**[25].

The main purpose of the irradiation of reference particles is the comparison between loose coated particles and coated particles in spherical fuel elements or prismatic compacts. Informations about the behaviour of the particles are usually obtained during irradiation by measuring the release of fission gases. The particles for these test come exclusively from production charges of the NUKEM.

The reference tests forTHTR - and KWSH-particles are plotted in the diagram together with the maximum design values of fast neutron dose and burn-up for the HTR's (AVR, KWSH and THTR). The symbols for the tests distinguish between tests a) loose particles, b) particles in spheres and c) in prismatic compacts. The numbers indicate the number of different sorts of particles or of spheres or compacts. The letters stand for the type of experiment and the reactor station. So is for example particles (P) in the FRJ-2 at Jülich (J).

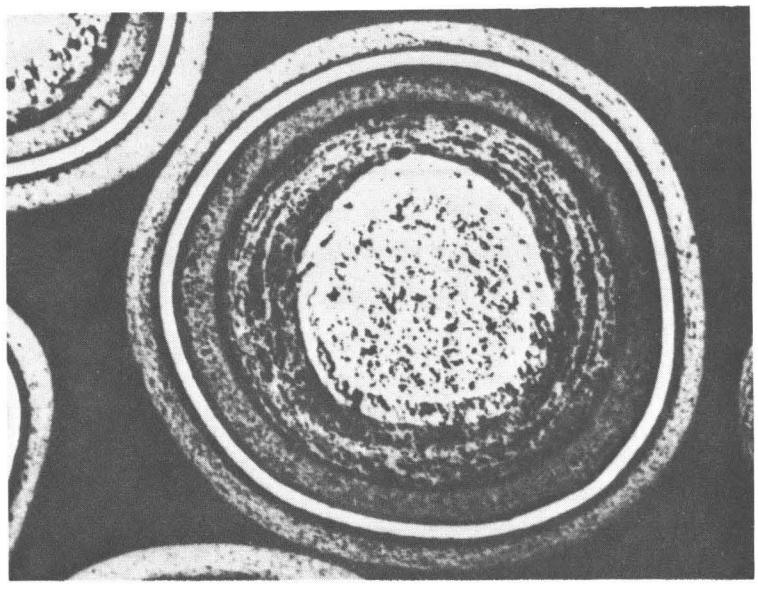
Other tests are performed in the BR-2 at Mol, in the R-2 at Studsvik, in the DRAGON reactor at Winfrith and in the DFR at Dounreay.

Results from irradiations of particles which reached the THTR specification are not yet available. From fission gas release measurements, however, it can be concluded that so far no difficulties have arisen. In principle coated particles can endure the conditions of the HTR specifications as proved by American irradiation tests.

Micrographs of a polished section of two reference particles for the PSC-reactor at Fort St. Vrain, which have reached a burnup of 22 and 27 % fima and a fast neutron dose of $1.6\text{-}1o^{21}$ and $8.4.1o^{21} n.cm^{-2}$, are shown in fig. 19. These achieved values are higher than the values specified for the THTR[26].

Reactor	PSC (Fort-St. Vrain/USA)				DRAGON (England)	KWSH (Geesthacht/BRD)	THTR (Schmehausen/BRD)
Fuel cycle	feed		breed		low enriched	U,Th	U,Th
Fuel composition	$(Th,U)C_2$ Th:U-235=4,25		ThC_2		UO_2	$(Th,U)O_2$ (Th:U-235 = 8	$(Th,U)O_2$ (Th:U-235 = 5
Diameter of kernel (μm)	200 ± 75		400 ± 100		800	600	400
Coating	BISO	TRISO	BISO	TRISO			
Buffer layer (μm)	50	50	50	50	30	45	60
HDI (High density-isotropic layer)	70	20	70	20	50	50	110
SiC		20		20	35	35	-
HDI		30		40	45	40	-
Irradiation:							
T_{max} (°C)	1260		1260		1250	1300	1250
max. burn-up (% fima)	20		7		8	10,4	14
max. fast neutron dose ($n.cm^{-2}$) ($E \geqslant 0{,}1$ MeV)	$9 \cdot 10^{21}$		$9 \cdot 10^{21}$		$8 \cdot 10^{21}$	$5 \cdot 10^{21}$	$6{,}4 \cdot 10^{21}$

Table 3: Reference particles for High Temperature Reactors



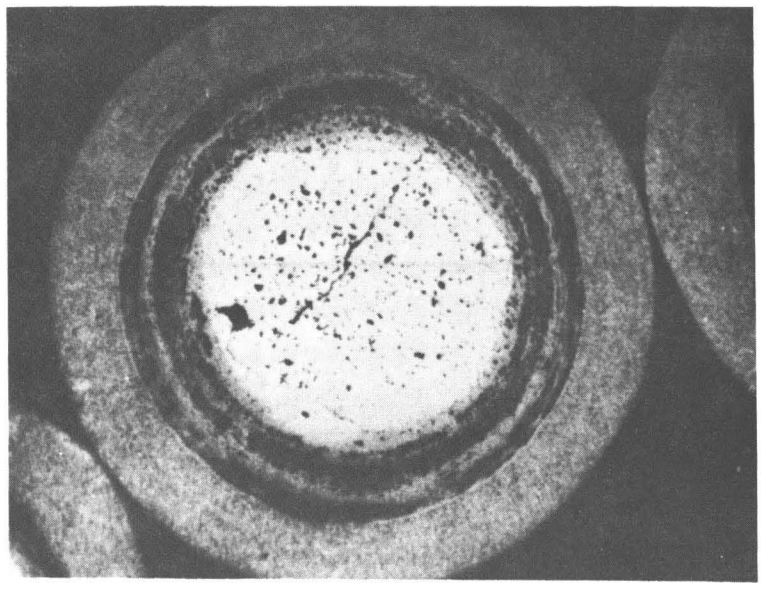
TRISO

27% FIMA

1300°C (MAX)

8.7×10^{21} NVT

M251-94 (P20) 175X



BISO

22% FIMA

1300°C (MAX)

8.4×10^{21} NVT

M275-48 (P18) 200X

Fig. 19: Irradiated coated particles from a GAA[26] specification test

5.2 Irradiations of model coated particles

Irradiation experiments performed on model particles are plotted in fig. 18. The particles are irradiated either in a high fast neutron flux (DN experiments in the DFR) or high burn-ups are reached with low fast doses (JP-experiment in the FRJ-2) or both high dose and burn-up are realized simultaneously (MOPS experiments in the BR-2 at Mol).

The aim of a fast neutron irradiation in the DFR is to determine the neutron dose causing failures of the coated particles by the built-up of neutron-induced stresses in the coatings. Theoretical evaluations are checked which are based upon the coated particles models developed by Scott and Prados (ORNL)[27,28], Kaae[29,30] and Walther (Sorin)[31,32]. These calculations are using the following data: geometrical data of the coated particles of spherical symmetry, material properties of the PyC- (and SiC-) coatings, burnup and fast **neutron dose.**

For checking the predicted irradiation behaviour, very carefully characterized coated particles are irradiated and the time of failure is determined. The comparison between theory and experiment should lead to a better understanding of the irradiation behaviour of the particles and therefore it is necessary to know thoroughly the properties of the various particle types. These demands pre-suppose that highly sophisticated measurement methods are at hand. Therefore, some important characterisation methods have been taken up in the Institut für Reaktorwerkstoffe (IRW) of KFA-Jülich - some have been improved, resp. developed for this purpose[33-36]. It is possible to measure the following properties of pyrocarbon by these methods (partially even after neutron irradiation): density, crystallite size, dimensional changes parallel and vertical to the direction of deposition, BACON-anisotropy factor, youngs modulus and tensile strength. Classification methods have been developed for assorting particles for irradiation experiments with definite diameters and sphericity.

.2.1 Fast neutron-induced irradiation defects on pyrocarbon
(Irradiation experiments DN II at Dounreay)

Fourty different sorts of coated particles have been irradiated in the DFR at about 1300°C to a fast neutron dose of $1.6 \cdot 10^{22}$ n.cm^{-2} (E > 0.1 MeV). This value is 2.5 times higher than the THTR specification. The achieved burnup was negligibly low (about 1 % fima). Most of the irradiated particles consisted of UC_2 kernels with a diameter of 400 µm and a duplex PyC coating consisting of a porous inner layer and a high density outer layer. The coating thickness, the initial density, the crystallite size and the orientation anisotropy have been systematically varied[37].
Due to its internal strength the inner porous layer causes a mechanical decoupling between the kernel and the outer layer. It is important for stopping the recoil atoms and it takes up fission gases in its pores. The dense outer layer serves as a pressure vessel and as a diffusion-barrier for gaseous and solid fission products. During irradiation stresses are built up in these layers which can lead to failures of the coatings. One of the main reasons for these stresses are anisotropical dimensional changes of the PyC induced by fast neutrons.
In the Dounreay-II experiment (DN II) the dimensional changes of PyC have been measured on irradiated flat PyC discs parallel and vertical to the deposition plane. The initial density and orientation anisotropy of the PyC had been varied[17]. The effect of fast neutrons upon anisotropic pyrocarbon layers are shown in figs. 20 a and b, parallel and vertical to the deposition plane.

In the DN-II experiment all particle coatings with PyC densities higher than 1.95 g/cm^{-3} were destroyed. Considering the orientation anisotropy as well it was found that the BAF of all particles which survived was smaller than 1.05. From the fragments of destroyed particles the following mechanism for the destruction of particles can be assumed. The fracture starts at one point of the outer surface of the particle, the crack propagates to the inner surface of the coating and fissures run starshapedly like degrees of longitude through the coating.

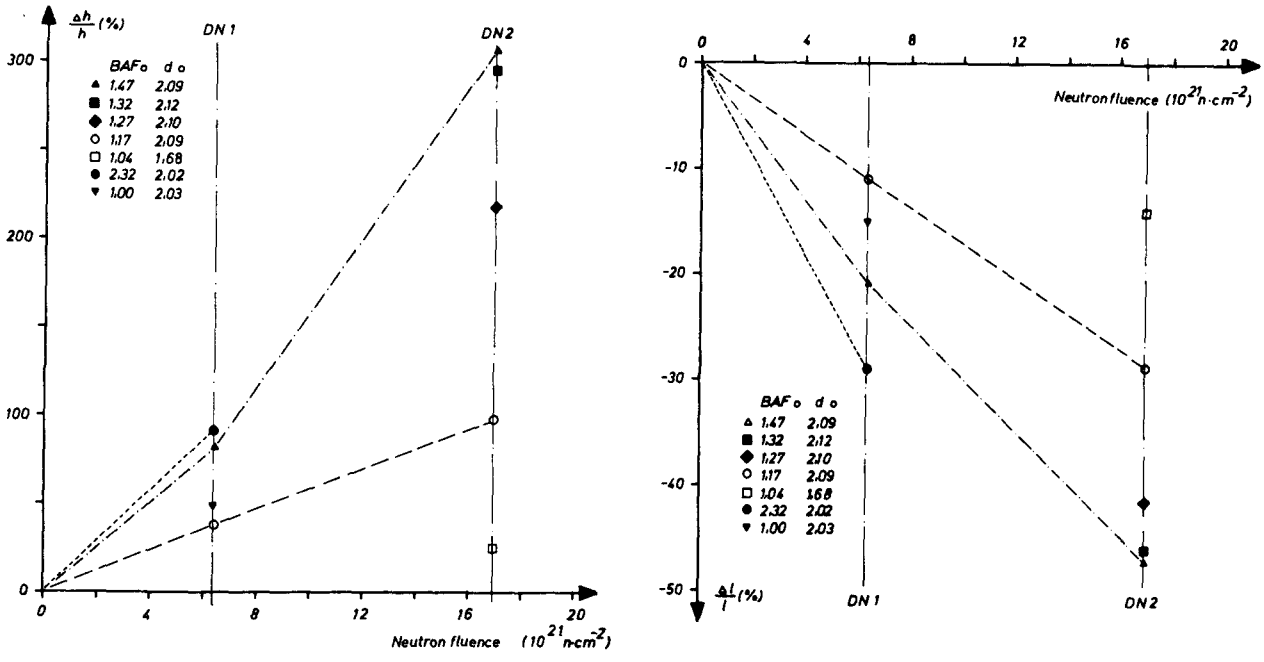


Fig. 2o a,b: Relative dimensional changes:
a) perpendicular to the deposition plane of
b) parallel the PyC layer with different orientation anisotropy as a function of the fast neutron dose (E ⩾ o.1 MeV)

Irradiation temperature: 135o ± 1oo°C

d_o: Apparent density before irradiation (g/cm^3)

BAF_o: BACON-anisotropy factor before irradiation

The result is a figure, which looks like an unfolding blossom (fig. 21). The crack formation releaves the stresses, and the pyrocarbon now continues to deform nearly stress free.
The thickness of the PyC-layer increases with increasing fast neutron dose, whereas it shrinks in the tangential direction.
Two particle-species, which were destroyed at two different fast neutron irradiation doses are shown in fig. 22. It has already been mentioned that all particle species with densities from 1.75 to 1.95 g/cm^3 and BAF ⩽ 1.o5 survived a fast neutron fluence 2.5 times higher than specified for the THTR.

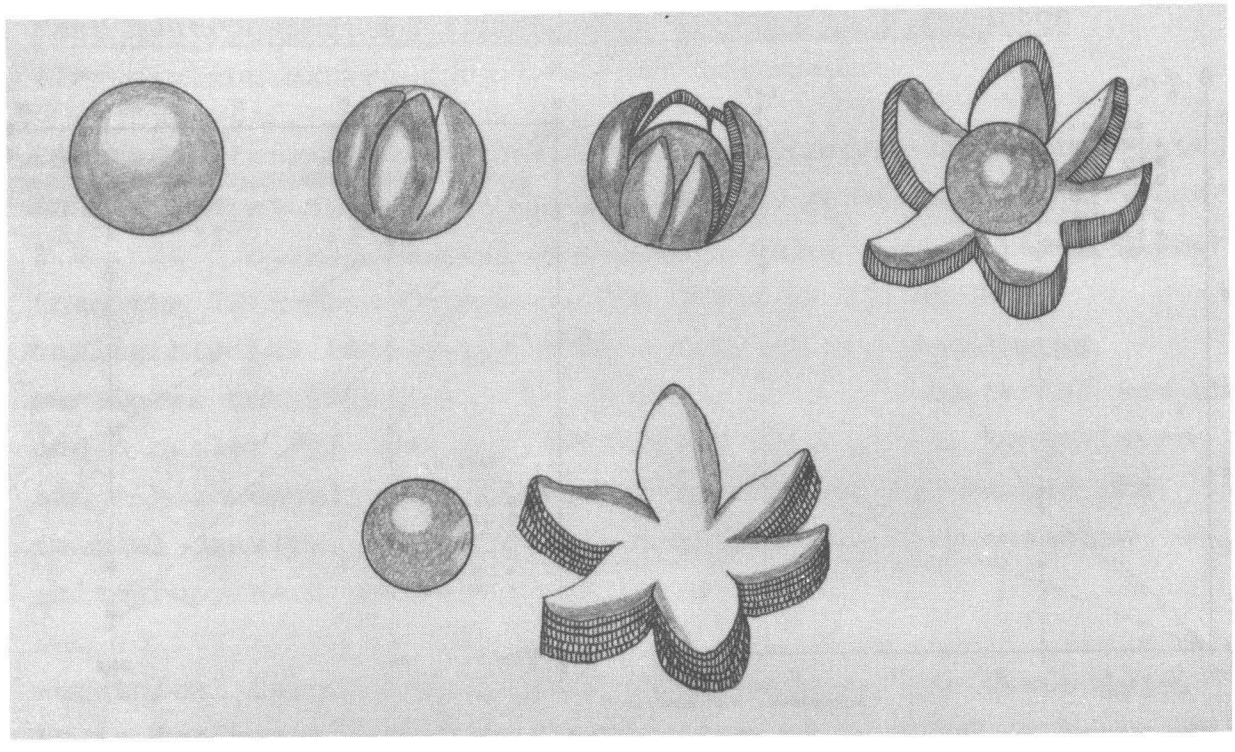


Fig. 21: Failures of coated particles caused by radiation induced dimensional changes (schematically)

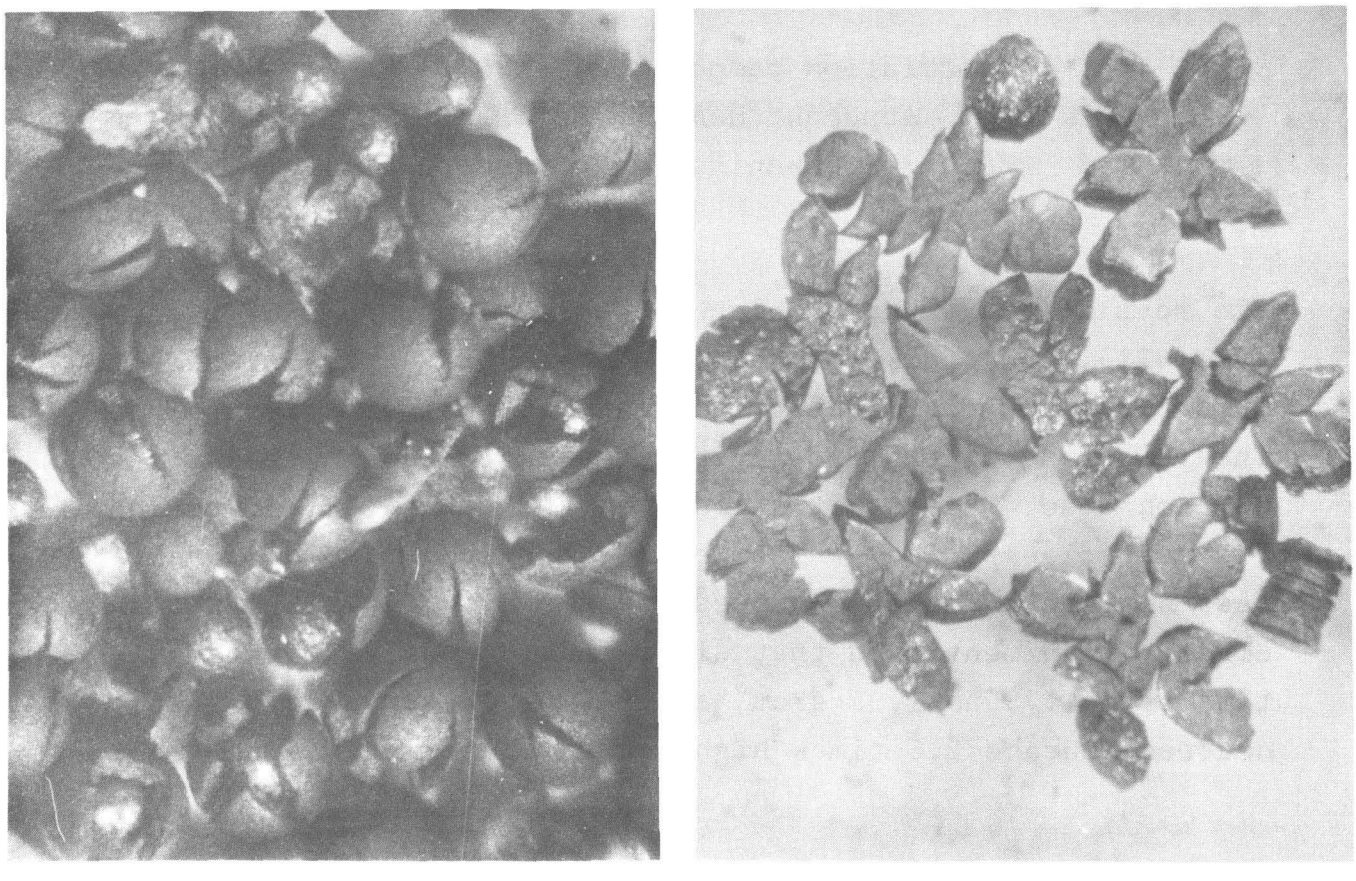


Fig. 22: Failures of coated particles caused by radiation induced dimensional changes

5.2.2 Investigations on the amoeba effect
(Irradiation experiment JP 8)

In the following an effect will be discussed which occurs when coated oxide or carbide particles are irradiated while located within a temperature gradient resulting in an unsymmetrical temperature distribution across the particle. In an experiment particles deliberately have been irradiated under extreme conditions in order to obtain in a short period of time first result on the behaviour of particles with large kernels[38]. The diameter of the oxide kernels ranged between 7oo and 9oo/um, the enrichment was 93 % U-235. They had been coated with a triplex PyC-coating, and were irradiated in the FRJ-2 at Jülich. The burn-up was 4 % fifa. Post-irradiation examination indicated that the central temperature had exeeded 18oo°C. Already afterthree days of irradiation a high-fission gas activity in the sweep-circuit indicated the **failure** of the coatings. After dismantling the capsules it was found that the kernel material had penetrated the coating so that empty coatings shells could be observed. Particles which appeared intact from the outside revealed in the metallographical examination that an extensive reaction between kernel and coating had occured. The oxide kernel was situated no longer in the centre of the particle but had migrated into the PyC coating (fig. 23). This effect is **already** known and is called amoeba effect[38-41]. Amoeba effects have been observed on carbide as well as on oxide U, Th- or U,Pu particles. The coating does not seem to have a restraining effect on the migration because the kernel moves as fast through layers of PyC as through layers of SiC. There are some contradictory explanations for this effect. However it is certain that the mechanism for the migration of oxide kernels is different **from that of carbide kernels. The amoeba effect on oxide kernels only has been observed on irradiated particles contrary to carbide kernels[41]. For a better understanding of this effect special irradiation experiments are carried out at Jülich and in other laboratories. The amoeba effect was found to be not necessary correlated with high irradiation temperatures. In experiments with moulded spherical fuel elements irradiated with central particle temperatures of 18oo and 2ooo°C no**

amoeba effect occured. Consequently, an early occurence of the amoeba effect only can be expected when at high irradiation temperature the temperature distribution is asymmetrical across the particles.

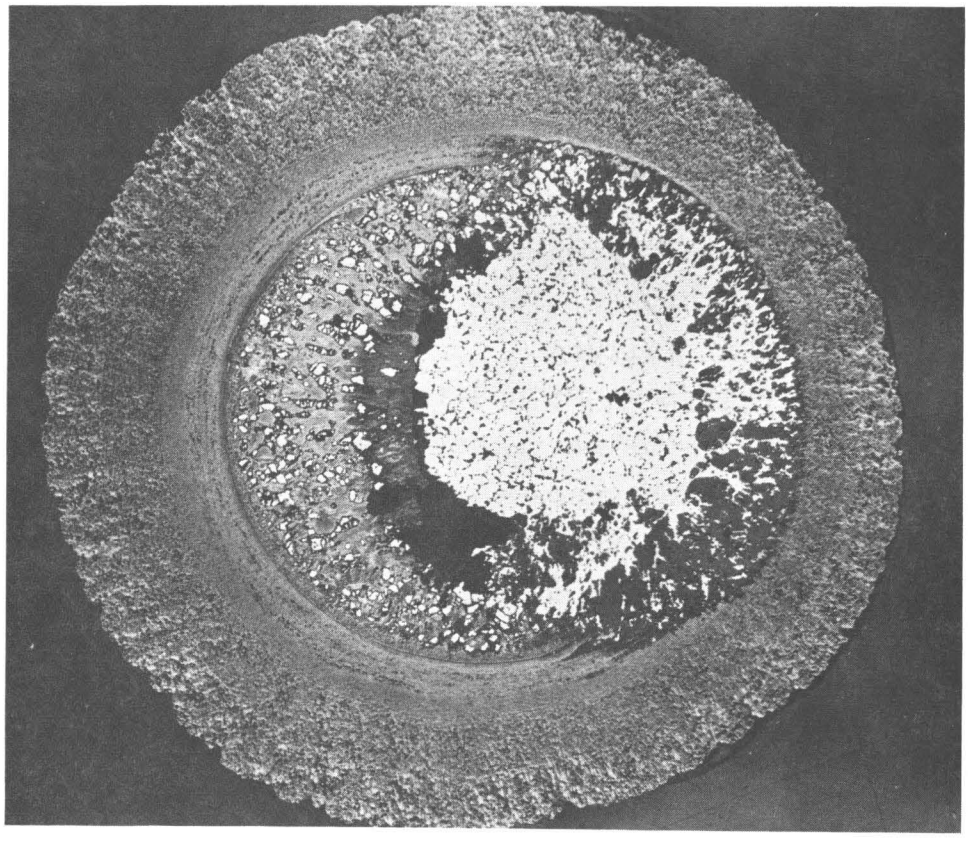


Fig. 23: Amoeba effect (JP-8-experiment) (UO_2-kernel (Ø 700-900 µm) 90 % enrichment; Pyrocarbon triplex coating; burn-up 4 % fima; Irradiation temperature >1600°C; power of one particle ~7 W

6. Summary

In this report the investigations on coated particles have been described, which are performed in the Institut für Reaktorwerkstoffe at Jülich in close collaboration with other institutes of the research center, foreign research centers and the German industry.
Summarizing a preview of the future work on coated particles in the frame of the HTR-material development shall be given, based on the present knowledge.
1. It is not necessary to develope new methods for the production of kernels from solutions. The future work must be restricted to the development of the present processes from the laboratory scale to the technical scale. Cost estimates will certainly play an important role for the process to be employed. The problems of the production of kernels with definite porosity is not completely solved and needs further work. An important question is the feasibility of the wet processes for producing kernels from reprocessed irradiated fuels, and their application in connection with a reprocessing cycle.
2. In the frame of production of PyC and SiC coatings with definite properties, large fluidized beds do not yet work fully satisfactory. The problem of non-spherical particles is caused by uncontrolable irregularities in the flow behaviour of the particles in the bed. Fluidized bed model studies indicated that the deviation from the sphericity of the particles could be minimized by the use of special nozzles resulting in different patterns of particle movement inside the fluidized beds[42].
As far as methods of characterisation are concerned, improvements are required as a consequence of the high demands on coated particles. Apart from already discussed properties others like density, anisotropy factor, crystallite size, youngs modulus, tensile strength, non-crystalline fraction are to be measured.
A method to detect the non-crystalline fraction in PyC is at present being developed in the Institut für Reaktorwerkstoffe of KFA.

3. In the future the work concerning the heavy metal and fission product transport in the coating at reactor conditions as well as their retention in the kernel materials will be very important. A close collaboration with the Institut für Reaktorentwicklung of KFA and the industrial firms BBK, GHH, NUKEM and research establishments like SGAE-Seibersdorf (Austria), Sorin (Italy) and Dragon-Winfrith (England) is envisaged.
4. The importance of prismatic compacts for HTR fuel elements has been discussed. It was concluded that this work is at the very beginning in the Federal Republic of Germany and important questions concerning the choice of suitable binder materials and filler graphites, the optimalisation of the component proportions as well as of fabrication processes and irradiation behaviour are features of the future investigations.
5. The main effort of the KFA work on coated particles will be the study of the irradiation behaviour. In the near future irradiation test facilities will be available at Jülich, Mol, Studsvik and Dounreay. Very efficient automatic sweep- and control-gas circuits have been developed in cooperation with the Institut für Reaktorexperimente at Jülich and the reactor stations at Mol and Studsvik.
The aim of the future tests is the continuation of specification tests for the HTR's, with emphasis on new particle concepts with PyC deposited from propene and with standard SiC-coatings. Furthermore, numerous model particle tests are envisaged. The objects are the retention of solid fission products like Sr, Ba and Cs with regard to the kernel material, i.e. oxide or carbide and the influence of kernel porosity on the burnup behaviour and fission product retention. Supporting and steering this irradiation program are calculations based on theoretical models by Prados and Scott[27,28], Kaae[29,30] and Walther[31,32] with new kernel and coating combinations, the results of which are checked by irradiations with high fast neutron doses.

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